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# The Crystal Structure of Hydrazinium Dichloride, $N_2H_6Cl_2$*

JERRY DONOHUE† AND WILLIAM N. LIPSCOMB‡
*Department of Chemistry, California Institute of Technology, Pasadena, California*

(Received December 31, 1946)

Accurate values of the two parameters in the structure of crystalline hydrazinium dichloride have been determined by the x-ray diffraction method, with the use of one and two dimensional Fourier syntheses. The N−N separation in this crystal is 1.42A, and is equal to that in hydrazinium difluoride. This N−N distance is 0.05A shorter than in gaseous hydrazine. Each chloride ion forms hydrogen bonds with three nitrogen atoms, the structure consisting of a three dimensional network of N−H···Cl bonds. The angle N−N−H···Cl is 100°. The configuration of the $N_2H_6^{++}$ ions is *trans*. The differences between this structure and that of hydrazinium difluoride probably arise from the greater coordinating ability of the chloride ion as compared with that of the fluoride ion. The shortening of the N−N distance may be caused in part by the formal charges on the nitrogen atoms, although it seems certain that this formal charge effect is not of general validity.

THE crystal structure of hydrazinium dichloride was first investigated by Wyckoff,[1] who found that crystals of the substance belong to the space group $T_h^6-Pa3$, and that four molecules of $N_2H_6Cl_2$ are situated in the unit cube, with $a_0=7.89$A. Wyckoff, with the methods then available, was able to arrive at only approximate values of the two parameters necessary to determine the structure completely (excluding the hydrogen atoms). He described the structure as "a $CaF_2$ grouping in which the chlorine ions are displaced from the symmetrical $\frac{111}{444}$ positions by the dumb-bell shaped $N_2H_6$ groups."[2]

We have investigated this crystal by the x-ray diffraction method in order to determine the interatomic distances accurately. The N−N distance is of interest in connection with the as yet unsettled question of the effect of formal charge on interatomic distance. The N−H···Cl distance affords further information on hydrogen bonding between nitrogen and chlorine. The structure also provides interesting comparisons with those of hydrazinium difluoride[3] and methylammonium chloride.[4]

## EXPERIMENTAL

Eastman White Label hydrazinium dichloride was dissolved in dilute hydrochloric acid. Slow evaporation of the solution yielded tiny octahedra suitable for x-ray examination. Crystals not over 0.2 mm in greatest dimension were

* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 1109.
† Predoctoral Fellow of the National Research Council.
‡ Present address: School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota.
[1] R. W. G. Wyckoff, Am. J. Sci. 5, 15 (1923).
[2] R. W. G. Wyckoff, *The Structure of Crystals* (Reinhold Publishing Company, New York, 1931), p. 246. Two drawings of the structure are also to be found in this reference, p. 247.
[3] W. L. Kronberg and D. Harker, J. Chem. Phys. 10, 309 (1942).
[4] E. W. Hughes and W. N. Lipscomb, J. Am. Chem. Soc. 68, 1970 (1946).

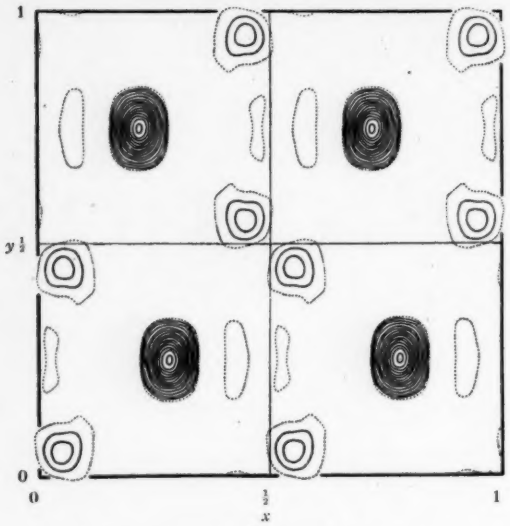


FIG. 1. Fourier projection on (001).

mounted on the x-ray goniometer heads in the usual way. Laue photographs showed that the symmetry class of the crystals was either $T$ or $T_h$. Oscillation photographs were taken with $CuK_\alpha$ radiation ($\lambda = 1.542$A) over the range required to give complete data for the zero, first, and second layer lines. In order to facilitate the visual estimation of intensities the multiple film technique was used.[5] The effect of absorption was ignored, since the size and shape of the crystals were favorable for doing so.

Measurement of the equatorial reflections on the oscillation photographs gave the value $a_0 = 7.87 \pm 0.01$A, in satisfactory agreement with Wyckoff's value of 7.89A. A very heavily exposed oscillation photograph showed no intermediate layer lines which would require the choice of a larger unit cell. The regular vanishing of $(hk0)$ when $h = 2n$, observed on the oscillation photographs, confirms Wyckoff's choice of the space group $T_h^6 - Pa3$. The observed density,[6] 1.4226, requires four (calculated 3.98) molecules of $N_2H_6Cl_2$ per unit cell. The eight nitrogen atoms lie in the positions[7] $\pm (uuu)$, $(\frac{1}{2}+u, \frac{1}{2}-u, \bar{u})$, $(\bar{u}, \frac{1}{2}+u, \frac{1}{2}-u)$, $(\frac{1}{2}-u, \bar{u}, \frac{1}{2}+u)$; and the eight chlorine atoms in a set of similar positions $\pm (vvv)$, etc.

For the calculation of $F$ values, the atomic scattering factors of James and Brindley[8] were used. The $f$ values for $N$ were increased by $2f$ of $H$ as an approximation to include the effect of the hydrogen atoms. All atomic $f$ values were multiplied by the temperature factor $\exp -\beta(\sin\vartheta/\lambda)^2$, and the value $\beta = 1.5$ was found to give satisfactory agreement between observed and calculated structure factors.

## DETERMINATION OF THE PARAMETERS

The approximate parameter values of Wyckoff, $u = 0.04$, $v = 0.27$, enable the assignment of signs to the $F$ values of all of the observed $(hk0)$ reflections. A Fourier projection on (001) made with the twenty-three available $(hk0)$ reflections is shown in Fig. 1. The smaller resolved peaks represent the nitrogen atoms; the larger peaks represent pairs of chlorine atoms which are too close together in this projection to be resolved. The symmetry of the cell, however, allows an accurate estimation of the chlorine parameter as well as the nitrogen parameter. The values $u = 0.052$ and $v = 0.278$ are indicated by this projection. It may be pointed out that the heights of the two kinds of peaks are in the ratio 3.9:1, whereas the ratio expected, $2Cl^-:NH_3^+$, is 36:9 = 4:1. The two small peaks and the asymmetry of the nitrogen peak (dotted in Fig. 1) undoubtedly arise from the omission of reflections which lie outside the limit of copper $K\alpha$ radiation.

TABLE I. Values of $F_{hk0}$.

| $(hk0)$ | $F_{obs}$ | $F_{calc}$ | $(hk0)$ | $F_{obs}$ | $F_{calc}$ |
|---|---|---|---|---|---|
| 200 | 4.1 | −7.8 | 630 | 5.5 | −5.9 |
| 210 | 3.4 | +3.5 | 640 | 2.4 | −2.1 |
| 220 | 7.3 | +13.4 | 270 | 1.0 | −1.2 |
| 230 | 4.9 | −5.2 | 650 | 1.3 | +1.3 |
| 400 | 5.9 | +7.9 | 800 | <0.4 | −0.7 |
| 410 | 5.5 | −6.9 | 810 | 4.8 | −4.9 |
| 420 | 5.4 | −5.3 | 470 | <0.4 | −0.1 |
| 430 | 2.8 | +2.1 | 820 | 1.1 | −1.5 |
| 250 | <0.4 | 0 0 | 660 | 1.2 | +1.1 |
| 440 | 4.3 | +4.1 | 830 | 3.3 | +3.2 |
| 600 | 3.8 | −3.8 | 840 | <0.4 | 0.0 |
| 610 | 4.9 | +5.1 | 670 | 1.7 | −1.8 |
| 620 | 2.3 | +2.1 | 850 | 3.1 | −2.9 |
| 450 | 4.7 | −4.3 | | | |

[5] J. J. deLange, J. M. Robertson, and I. Woodward, Proc. Roy. Soc. (London) **A171**, 398 (1939).

[6] H. Schiff and U. Monsacchi, Zeits. f. physik. Chemie **21**, 292 (1896).

[7] *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (Gebrueder Borntraeger, Berlin, 1935), Vol. I, p. 320.

[8] *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (Gebrueder Borntraeger, Berlin, 1935), Vol. II, p. 571.

Since both nitrogen atoms and chlorine atoms lie on a body diagonal of the unit cube, this crystal is well suited to the application of the Fourier method of calculating the electron density along a line. The general expression for the electron density as a function of the coordinates $x$, $y$, and $z$ simplifies for the case $x=y=z=d$ to

$$\rho(d)=K\sum_H A_H \cos 2\pi Hd,$$

where

$$A_H=\sum_{h+k+l=H} F_{hkl}.$$

In making this summation, all available ($hk0$), ($hk1$), and ($hk2$) data were used, the signs of all $F$ values being determined from the parameters obtained with the projection on (001). The use of equalities of the type $F_{hkl}=-F_{\bar{h}kl}$ for $h=2n$ or $k=2n$, etc., increased the number of known $F$ values to nearly 300. The reflections were classified according to $h+k+l$, and the series was summed over $h+k+l=0$ to 15 from $d=0$ to $d=\frac{1}{2}$ in intervals of 0.004 in $d$. Both this summation and the projection on (001) were made with the use of punched cards and International Business Machines.[9] The density function $\rho(d)$, the curve labelled OBS in Fig. 2, gives the values $u=0.052$ and $v=0.279$, which are in excellent agreement with the values given by the (001) projection.

TABLE II. Value of $F_{hkl}$.

| ($hkl$) | $F_{obs}$ | $F_{calc}$ | ($hkl$) | $F_{obs}$ | $F_{calc}$ | ($hkl$) | $F_{obs}$ | $F_{calc}$ |
|---|---|---|---|---|---|---|---|---|
| 111 | 4.3 | +6.0 | 261 | 5.3 | −5.4 | 812 | 3.9 | +3.9 |
| 211 | 2.4 | −1.8 | 541 | 1.3 | −1.4 | 182 | 0.4 | +0.4 |
| 221 | 4.3 | −4.5 | 451 | 3.5 | +3.2 | 742 | <0.4 | +0.6 |
| 311 | 2.1 | +2.6 | 622 | 2.8 | −3.0 | 472 | 1.3 | −1.5 |
| 222 | 5.1 | −6.3 | 542 | 0.6 | +0.6 | 822 | <0.4 | −0.3 |
| 321 | 1.4 | −1.3 | 452 | 0.7 | +0.9 | 661 | 1.6 | −1.7 |
| 231 | 1.5 | +1.3 | 631 | 2.5 | +2.3 | 831 | 2.5 | −2.3 |
| 322 | 1.2 | +1.1 | 361 | <0.4 | −0.5 | 381 | 1.0 | −1.1 |
| 411 | <0.4 | 0.0 | 632 | 3.1 | +2.9 | 751 | 0.6 | +0.7 |
| 331 | 0.4 | +0.7 | 362 | 1.1 | +1.1 | 662 | 0.7 | −0.7 |
| 412 | 4.4 | +4.4 | 711 | 0.6 | −0.8 | 832 | 3.9 | −3.7 |
| 142 | 2.0 | +2.0 | 551 | 0.7 | −0.6 | 382 | <0.4 | +0.4 |
| 332 | 2.6 | −2.1 | 641 | 2.0 | +1.8 | 752 | 1.4 | +1.4 |
| 422 | 5.1 | +5.8 | 461 | 3.7 | +3.4 | 572 | <0.4 | +0.3 |
| 431 | 3.0 | −3.1 | 721 | 0.6 | −0.6 | 841 | <0.4 | 0.0 |
| 341 | 3.2 | −2.9 | 271 | 2.0 | +2.0 | 481 | 3.1 | −3.1 |
| 511 | 0.6 | −0.3 | 552 | 0.7 | −0.8 | 911 | 1.0 | −1.2 |
| 432 | 4.6 | −5.6 | 642 | 1.7 | +1.6 | 842 | 0.5 | −0.5 |
| 342 | 2.6 | −2.0 | 722 | <0.4 | 0.0 | 921 | <0.4 | −0.1 |
| 512 | 2.4 | −2.0 | 731 | 1.0 | −1.0 | 291 | 1.2 | −1.2 |
| 152 | 1.5 | −1.8 | 651 | 3.8 | −3.4 | 761 | 0.4 | −0.5 |
| 441 | 3.9 | −3.5 | 561 | 1.8 | −1.7 | 671 | 3.6 | +3.4 |
| 552 | 2.5 | −2.5 | 732 | 1.3 | −0.9 | 762 | 0.4 | −0.4 |
| 531 | 0.6 | +0.4 | 372 | 0.6 | −0.6 | 672 | <0.4 | +0.3 |
| 442 | 3.4 | −3.4 | 652 | 3.4 | −3.4 | 922 | <0.4 | 0.0 |
| 532 | 1.5 | +1.7 | 562 | <0.4 | −0.2 | 851 | 3.3 | +2.9 |
| 352 | <0.4 | 0.0 | 811 | 0.6 | +0.6 | 581 | <0.4 | −0.1 |
| 611 | 1.7 | −1.6 | 741 | 1.0 | −1.1 | | | |
| 621 | 0.8 | −0.8 | 471 | 2.5 | −2.6 | | | |

[9] P. A. Shaffer, Jr., Verner Schomaker, and Linus Pauling, J. Chem. Phys. **14**, 648 (1946).

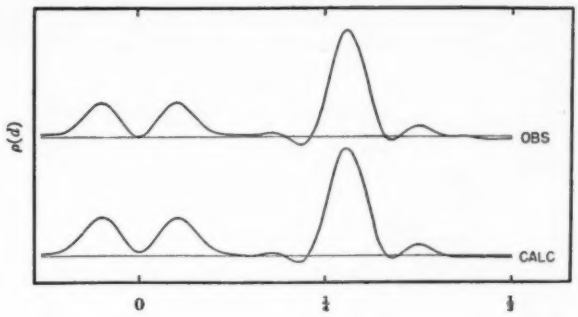


FIG. 2. Electron density along the line $x=y=z=d$.

Since data obtained only from the zero, first, and second layer lines were used, no reflections for which $h$, $k$, and $l$ were each $>3$ were included in the calculation of the function $\rho(d)$. Although this function apparently was satisfactorily convergent, the effect of the missing spectra on the positions of the maxima was not known. For this reason, we calculated a second density function, using, in place of the observed $F$ values, a set of $F$ values calculated for a structure in which $u=0.052$ and $v=0.278$. The same terms were omitted in the calculation of this second density function as were omitted in the calculation of the first. The resulting curve, labelled CALC in Fig. 2, shows maxima at $u=0.052$ and $v=0.278$. The omission of terms of high order in $h$, $k$, and $l$ did not lead to parameters which were significantly different from those which were assumed, and we may, therefore, infer that the parameters obtained with the observed data are a correspondingly accurate representation of the atomic positions in the crystal.

Since there have been cases in which the inclusion of the scattering of the hydrogen atoms led to a significant improvement in the agreement between observed and calculated values of $F_{hkl}$,[10] we recalculated all $F_{hkl}$ with $\sin\vartheta/\lambda<0.30$, placing the twenty-four hydrogen atoms in the general positions[9] of $Pa3$ with $x=0.108$, $y=0.039$, and $z=0.126$. These values place groups of three hydrogen atoms 1.03A from each nitrogen atom, on lines between the nitrogen atom and its closest chlorine neighbors. The over-all effect was a very small improvement of doubtful significance.

[10] For example, H. A. Levy and R. B. Corey, J. Am. Chem. Soc. **63**, 2095 (1941). Cf. also reference 6.

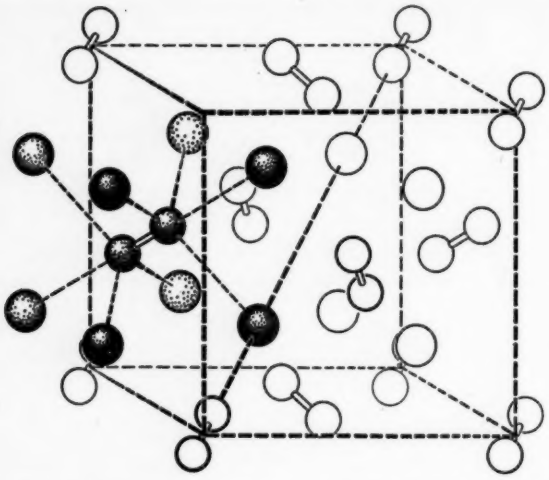

FIG. 3. One unit cell of the crystal, showing the environment of one $N_2H_6^{++}$ group, and the body diagonal along which $\rho(d)$ was determined. The large balls represent chloride ions, the small balls, nitrogen atoms.

The above results lead us to the parameter values $u=0.052$ and $v=0.279$. We believe it very unlikely that either of these parameters is in error by more than $\pm 0.0015$.

The agreement between observed and calculated values of $F$ is shown in Tables I and II. It is probable that the very strongest reflections, *viz.*, (200), (220), (400), (410), (111), and (222), which are all observed to be too weak, are subject to extinction.

## DISCUSSION

The values of the parameters lead to the following interatomic distances: the N−N distance within the hydrazinium group is 1.42A, and from the limits of error given for this parameter it is very unlikely that this distance can be in error by more than ±0.04A. A drawing of the structure showing the environment of one $N_2H_6^{++}$ group is shown in Fig. 3. Each nitrogen atom has four closest chloride neighbors, one (type I) lies at 3.10A±0.04A on an extension of the line through the two nitrogen atoms, the other three (type II), also at 3.10±0.02A, form a triangular pyramid with the nitrogen atom, the angles N−N···Cl being 100°±2°. Each chloride ion has four nitrogen neighbors, one of type I and three of type II, and in addition six chloride neighbors which form the equilateral triangle are connected to the nitrogen atom by hydrogen bonds; the configuration of the $N_2H_6^{++}$ is staggered or *trans*.

It is of interest to compare in detail the structure of $N_2H_6Cl_2$ with that of $N_2H_6F_2$.[3] In both crystals the halide ions form hydrogen bonds leading to N−H···X distances which are shorter than the sums of the respective ionic radii,[11] 0.11A shorter in the chloride and 0.14A shorter in the fluoride. In both crystals a nitrogen atom has four closest halide neighbors, three of which are hydrogen bonded, and one of which lies on the extension of the N−N axis. In $N_2H_6Cl_2$, this fourth chloride ion lies the same distance from the nitrogen atom as do the other three chloride ions, whereas in $N_2H_6F_2$ the fourth fluoride ion lies at a distance 0.18A greater than do the other three. This N···F distance is approximately the sum of the ionic radii. The angle N−N···X is 100° in $N_2H_6Cl_2$ and 110° in $N_2H_6F_2$. The smaller angle and the equality of the four N−H···X distances in the chloride suggest that the fourth chloride ion is subject to significant attraction by the three hydrogen atoms, a situation not unlikely if the actual value of the angle N−N−H is closer to the tetrahedral value 109° 28′. In both crystals a halide ion has four nitrogen neighbors. In $N_2H_6F_2$, a fluoride ion has, in addition, three closest fluoride neighbors, at distances 0.68A greater than the sum of the ionic radii, so that the structure essentially does not depend on any F···F contacts. In $N_2H_6Cl_2$, on the other hand, a chloride ion has six closest chloride neighbors, at distances only 0.36A greater than the radius sum. It is possible that Cl···Cl contacts are of some importance in determining this structure. The major difference between the two structures then arises from the greater coordinating ability of chloride ion as compared to that of fluoride ion. The configuration of the $N_2H_6^{++}$ ion is *trans* in both crystals.

The N−H···Cl distance of 3.10A may be compared with the N−H···Cl distance of 3.18A found in $NH_3CH_3Cl$.[4] In the latter crystal, the $CH_3-NH_3$ groups are probably rotating, and furthermore only three hydrogen bonds are

[11] An ionic radius of one $-NH_3^+$ group of the hydrazinium ion may be taken equal to the ionic radius of 1.54A for $NH_4^+$, observed in $NH_4Br$ and $NH_4Cl$. This value leads to an ionic radius of 1.41A when corrected to coordination number 4.

formed, on the average, between a nitrogen atom and four chloride ions. These differences lead to much weaker and consequently longer N−H···Cl bonds in methylammonium chloride.

The N−N distance in both hydrazinium dichloride and hydrazinium difluoride is the same, 1.42A. This distance is 0.05A shorter than the N−N distance in gaseous hydrazine.[12] This shortening has been attributed to the formal charges on the nitrogen atoms.[3] However, since the structure of the $N_2H_6^{++}$ ion for which there are adjacent charges on each nitrogen atom contributes but 25 percent to the normal state of the ion,[3] it seems essentially illogical to attribute a shortening of this magnitude to the formal charges. The formal charge effect, as originally conceived,[13,14] was intended to correct the covalent radius of an atom which had a formal charge of +1 by about −0.03A. Some molecules in which this effect might be expected, together with the available experimental data, are presented in Table III. Because of the uncertainty involved in predicting distances which are involved in single-bond double-bond resonance, only single covalent bonds are included in the table. The predicted distances are those in the table of revised covalent radii of Schomaker and Stevenson.[15]

TABLE III.

| Bond | Compound | Observed distance | Predicted distance* |
|---|---|---|---|
| $O-N^+$ | $HNO_3$ | 1.41±0.02A[a] | 1.43A |
| $C-N^+$ | $C(NO_2)_4$ | 1.47±0.02A[b] | 1.46A |
| | $CH_3NH_3Cl$ | 1.46±0.01A[c] | |
| | $(CH_3)_3NO$ | 1.49±0.02A[d] | |
| $N^+-N^+$ | $N_2H_6F_2$ | 1.42±0.02A[e] | 1.47A |
| | $N_2H_6Cl_2$ | 1.42±0.04A[f] | |
| $C-S^+$ | $(CH_3)_2SO$ | 1.84±0.02A[d] | 1.81A |
| $C-S^{++}$ | $(CH_3)_2SO_2$ | 1.81±0.02A[d] | 1.81A |

* Reference 15 in text.
[a] L. R. Maxwell and V. M. Mosley, Phys. Rev. **57**, 1079A (1940).
[b] A. J. Stosick, J. Am. Chem. Soc. **61**, 1127 (1939).
[c] Reference 4 in text.
[d] R. E. Rundle, Dissertation, California Institute of Technology (1941).
[e] Reference 3 in text.
[f] This determination.

It is apparent that the correction for formal charge is not generally applicable. There do not seem to be sufficient experimental data concerning this point so that a satisfactory revision of the original correction can be made. X-ray investigations of a hydroxylammonium salt such as $NH_3OHCl$ and of a metallic peroxide would provide additional information of interest.

[12] P. A. Giguère and V. Schomaker, J. Am. Chem. Soc. **65**, 2025 (1943).
[13] N. Elliott, J. Am. Chem. Soc. **59**, 1380 (1937).
[14] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition, p. 171.
[15] V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. **63**, 37 (1941).

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# Infra-Red Absorption Spectra of the $C_2$ to $C_4$ Mono-Olefins and of 2-Methyl-2-Butene

R. S. RASMUSSEN AND R. ROBERT BRATTAIN
*Shell Development Company, Emeryville, California*

(Received October 28, 1946)

The infra-red absorption spectra from 2 to 15$\mu$ of ethylene, propylene, 1-butene, *cis*-2-butene, *trans*-2-butene, isobutene, and 2-methyl-2-butene in the vapor state have been obtained. Features common to all the spectra are discussed and their aid in determining the structure of new compounds is pointed out. The fundamental frequencies and vibrational assignments of ethylene and propylene are discussed.

## I. INTRODUCTION

DURING the last few years there have been several investigations of the infra-red absorption spectra of higher paraffin hydrocarbons ($C_3$ to $C_8$, principally).[1] This paper reports a complementary survey of the vapor spectra of the $C_2$ to $C_4$ olefins and of one $C_5$ olefin, 2-methyl-2-butene. These spectra were obtained both for their general spectroscopic and molecular-structural interest, and also for use in the infra-red spectrophotometric analysis of hydrocarbon mixtures.[2]

The spectrum of ethylene has been the subject of many investigations, principally under high resolution with gratings,[3] and the wave-lengths of its absorption maxima have been accurately determined. The purpose in redetermining this spectrum with a high-resolution prism instrument was to get a more accurate idea of the intensities of absorption than is obtainable with a grating, and to check the wave-length calibration of the spectrograph used in this work.

Other salt-prism work has appeared in the literature on the spectra of propylene,[4,5] 1-butene,[6] *cis*- and *trans*-2-butene,[7] mixed 2-butenes,[6] and isobutene.[6]

## II. EXPERIMENTAL

The spectra were obtained with the research infra-red spectrograph of this laboratory.[8] This instrument employs a rocksalt prism in a Wadsworth-Littrow mounting and automatically records a curve of wave-length against a first approximation of percent transmission. During a recording the energy is kept approximately constant throughout the 2$\mu$ to 15$\mu$ region by continuously and automatically opening the slits to compensate for the decrease of energy toward long wave-lengths. Transmission values were obtained from recordings of short sections of the spectrum with the same cell filled and empty, so that no corrections for cell absorption or reflection were necessary.

All spectra were obtained in a cell 15 cm long, at pressures indicated on the absorption curves. Each curve shown in the figures is the average

[1] B. L. Crawford, W. H. Avery, and J. W. Linnett, J. Chem. Phys. **6**, 682 (1938)—ethane.
F. Stitt, J. Chem. Phys. **7**, 297 (1939)—hexadeuteroethane.
V. L. Wu and E. F. Barker, J. Chem. Phys. **9**, 487 (1941)—propane.
S. E. Whitcomb, H. H. Nielsen, and L. H. Thomas, J. Chem. Phys. **8**, 143 (1940)—*n*-undecane.
W. H. Avery and C. F. Ellis, J. Chem. Phys. **10**, 10 (1942)—ethane, 2,2-dimethylbutane.
G. A. Stinchcomb, J. Chem. Phys. **7**, 853 (1939)—*n*-pentane.
J. J. Fox and A. E. Martin, Proc. Roy. Soc. (London) **A175**, 208 (1940)—some $C_7$ to $C_{34}$ hydrocarbons in 3$\mu$ region.
C. F. Kettering and W. W. Sleator, Physics **4**, 39 (1933)—various $C_5$ to $C_8$ hydrocarbons.
D. Barca-Galateanu, Bull. Soc. Roumaine Phys. [70], **38**, 109 (1938)—*n*-hexane, *n*-heptane, *n*-dodecane.
P. Lambert and J. Lecomte, Ann. de physique **18**, 329 (1932), and earlier work by these authors—some $C_6$, $C_7$, and $C_8$ hydrocarbons.
R. A. Oetjen, H. M. Randall, and W. E. Anderson, Rev. Mod. Phys. **16**, 260, 265 (1944)—all $C_8$ paraffins.
H. W. Thompson, J. Chem. Soc. 183 (1944)—2,2- and 2,3-dimethylbutanes.

[2] R. R. Brattain and O. Beeck, J. App. Phys. **13**, 699 (1942). R. R. Brattain, R. S. Rasmussen, and A. M. Cravath, J. App. Phys. **14**, 418 (1943).

[3] W. S. Gallaway and E. F. Barker, J. Chem. Phys. **10**, 88 (1942). This paper gives earlier references.

[4] E. B. Wilson, Jr. and A. J. Wells, J. Chem. Phys. **9**, 319 (1941).

[5] W. H. Avery and C. F. Ellis, J. Chem. Phys. **10**, 10 (1942).

[6] R. B. Barnes, U. Liddel, and V. Z. Williams, Ind. Eng. Chem., Anal. Ed. **15**, 83 (1943); W. W. McCarthy and J. Turkevich, J. Chem. Phys. **12**, 461 (1944).

[7] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 247 (1938).

[8] R. R. Brattain, Phys. Rev. **60**, 164 (1941).

of at least two runs at the indicated pressure. Because of galvanometer drift and slow heating effects inside the spectrograph, the transmission values are usually accurate to only 2.5 percent. In a few especially bad cases, principally at $\lambda > 12.5\mu$, the accuracy may be only 5 or 10 percent.

The wave-length range covered was $2\mu$ to $14.5\mu$ or $15.0\mu$ and the spectral slit widths‡ at various points in this interval are indicated by the distances between the short vertical lines at $3\mu$, $6\mu$, $9\mu$, and $12\mu$. The wave-length calibration of the spectrograph is empirical and is based on wave-lengths in the spectra of ammonia and carbon dioxide taken from grating work in the literature. Wave-length errors due to non-reproducibility are believed to be not greater than $\pm 0.01\mu$ for $\lambda > 5\mu$. At shorter wave-lengths the error increases, becoming $\pm 0.02$ at $\lambda = 3\mu$.

The sources and purities of the various hydrocarbons used are as follows:

*Ethylene.* The ethylene was Ohio Chemical Company product, containing, so far as all chemical information obtainable goes, no impurities other than small amounts of permanent gases. Gallaway and Barker,[3] using ethylene from the same source, found evidence of an impurity in a very weak band at $5.66\mu$, whose fine structure indicated that it was not due to ethylene. No band at this wave-length of sufficient intensity to be noticeable was observed in the present work, although a weak one may have escaped notice. In any case, the impurity indicated is certainly too small to affect the main features of the spectrum.

*Propylene.* The propylene used was made from di-isopropyl ether, and was specially redistilled. A cylinder of product representing a 20 percent heart cut was taken, and the sample used for the present work was drawn from this cylinder. The purity is believed to be better than 99.0 percent. Mass spectrometric analysis indicated 0.1 percent acrolein, and essentially no propane.

*1-Butene.* The sample of 1-butene was obtained from a pilot plant distillation of normal butylenes obtained from *sec*-butyl alcohol. Comparison with laboratory preparations of high purity indicated a probable purity of 99.3 percent.

*cis-2-Butene.* A large sample of 2-butene (approximately 75 percent *cis*, 25 percent *trans*) was distilled in a pilot plant still under high reflux, and a cylinder of high-boiling end taken which analyzed *circa* 95 percent *cis*-2-butene by standard spectrophotometric methods. Calibration standards for this analysis were obtained from Dr. W. E. Vaughan of these laboratories, and were part of the *cis*- and *trans*-2-butenes prepared at Harvard University.[9] The 95 percent material was redistilled in an 80-plate low-temperature laboratory column and several cuts were obtained which were spectrophotometrically indistinguishable in purity from the Harvard sample.

*trans-2-Butene.* A sample of 2-butene analyzing 85 percent *trans* form was redistilled in the same laboratory column as was used for the *cis*-2-butene. The best cut, which analyzed 99.6 percent *trans*-2-butene spectrophotometrically, was used for the present work.

*Isobutene.* The sample of isobutene used was made from *tert*-butyl alcohol and was distilled in a plant column. Standard gas analysis procedures and comparison with highly purified laboratory products indicated a probable purity of 99.6 percent.

Mass spectrometric examination of all these butene samples indicated that saturates were negligibly low (<0.1 percent).

*2-Methyl-2-butene.* The sample of 2-methyl-2-butene used was prepared from *tert*-amyl alcohol, and carefully distilled. Physical constants were: specific gravity (20/4), 0.6622; $n_D^{20}$, 1.3872.

## III. RESULTS

The absorption curves are shown in Figs. 1 to 7. Table I gives the observed wave-lengths and frequencies of the absorption maxima of ethylene from 12.3 to $15\mu$, since these have not been reported previously in the grating work referred to, although Thompson and Harris have shown a salt-prism curve of the peaks.[10] The observed

‡ These are the actual wave-length limits included by the slits; the effective slit widths or theoretical intervals which can be resolved are one half of these values. The resolution actually achieved is slightly better than the spectral slit widths, but is considerably poorer than the effective slit widths.

[9] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, J. Am. Chem. Soc. **57**, 876 (1935).

[10] H. W. Thompson and G. P. Harris, Trans. Faraday Soc. **40**, 295 (1944).

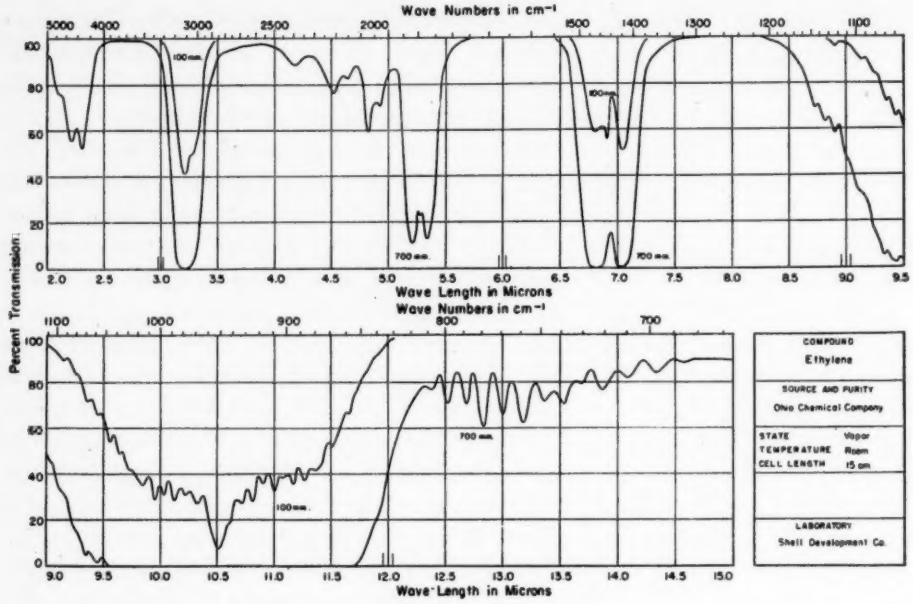


FIG. 1. Infra-red absorption spectrum of ethylene.

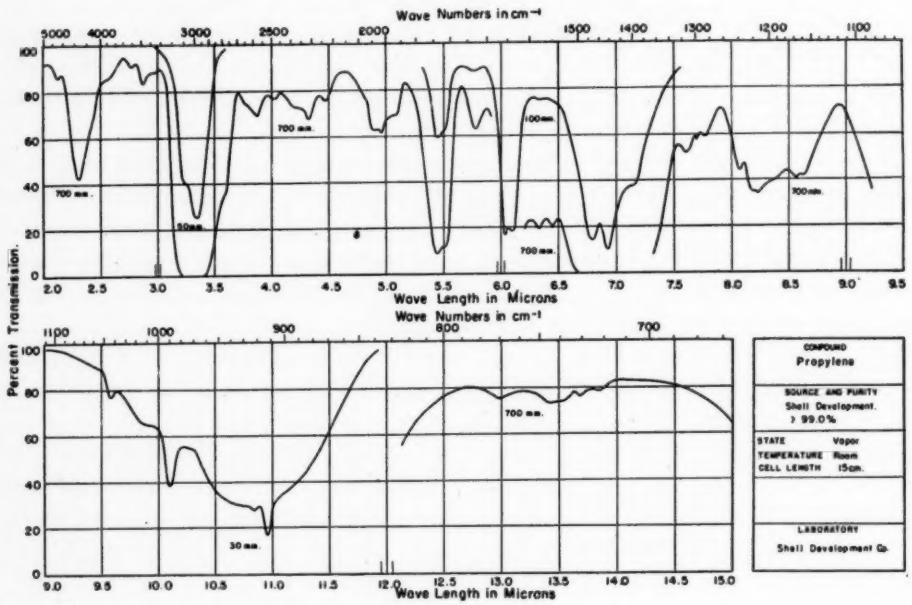


FIG. 2. Infra-red absorption spectrum of propylene.

wave-lengths, frequencies, and intensities of the absorption maxima of the other compounds are shown in Table II. The intensities given in these tables are taken from the spectra at 100 mm Hg pressure and are in units of 10 percent absorption; thus 0 indicates less than 5 percent absorption, 1 indicates between 5 and 15 percent absorption, etc. Estimated absorption due to tails of other bands has been subtracted in obtaining these values. Brackets indicate the intensity of a whole band, individual features of which are given by the wave-lengths enclosed. Bands of wave-length less than $5\mu$ have their frequencies rounded off to the nearest 5 $cm^{-1}$.

The spectra presented here show in general greater resolution than previously published curves (except, of course, in the case of ethylene). However, the earlier work is generally in good agreement with the present, with one exception: a moderately strong band at 1233 $cm^{-1}$ shown by

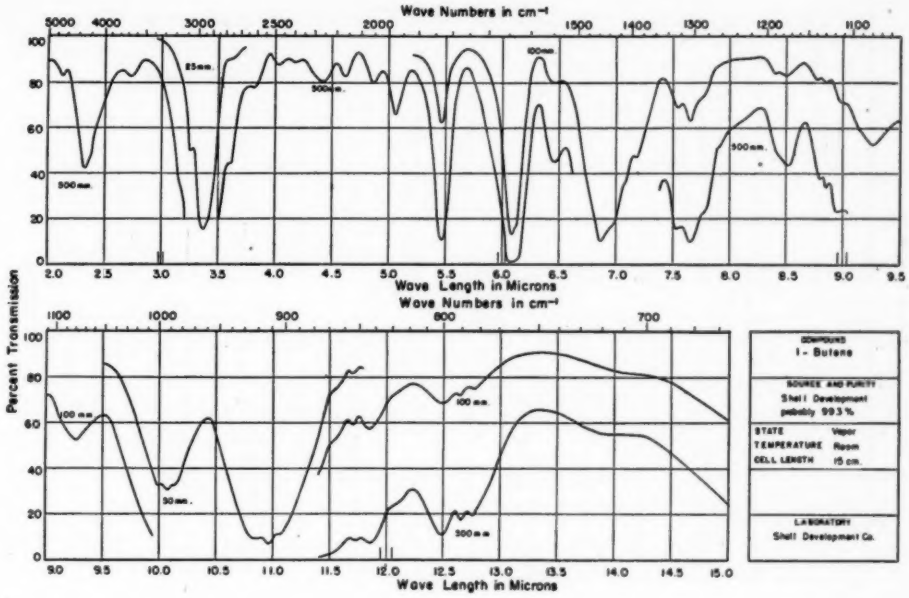


FIG. 3. Infra-red absorption spectrum of 1-butene.

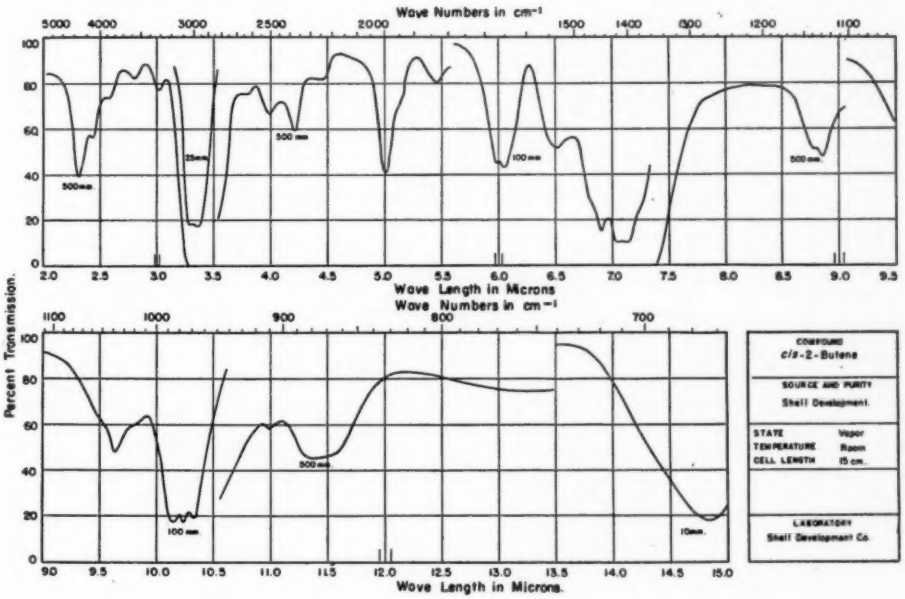


FIG. 4. Infra-red absorption spectrum of *cis*-2-butene.

Gershinowitz and Wilson[7] in the spectrum of *cis*-2-butene was not found in the present work.

## IV. GENERAL DISCUSSION

Aside from specific frequency assignments for individual molecules, several points of interest are to be noticed in the spectra of the olefins taken as a group. Many of these points have been noted also in recent articles by Thompson and Torkington.[11]

In the $3\mu$ region, the four molecules having the olefinic $CH_2$ group (ethylene, propylene, 1-butene and isobutene) show a band at *circa* $3.2\mu$ (3100 $cm^{-1}$), which in the case of all but ethylene appears as a shoulder on the strong band at *circa*

[11] H. W. Thompson and P. Torkington, Trans. Faraday Soc. **51**, 247 (1945); Proc. Roy. Soc. (London) **A184**, 3 (1945).

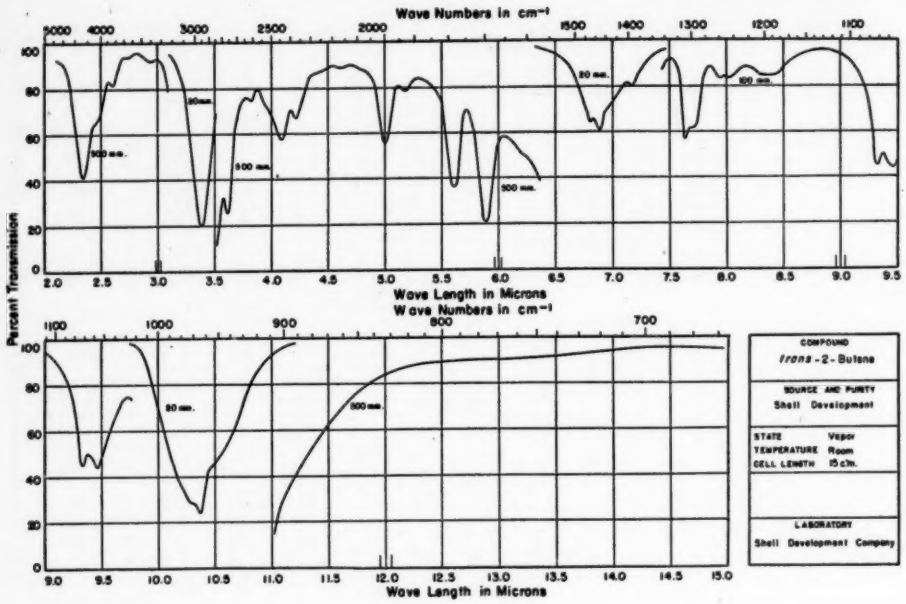


FIG. 5. Infra-red absorption spectrum of *trans*-2-butene.

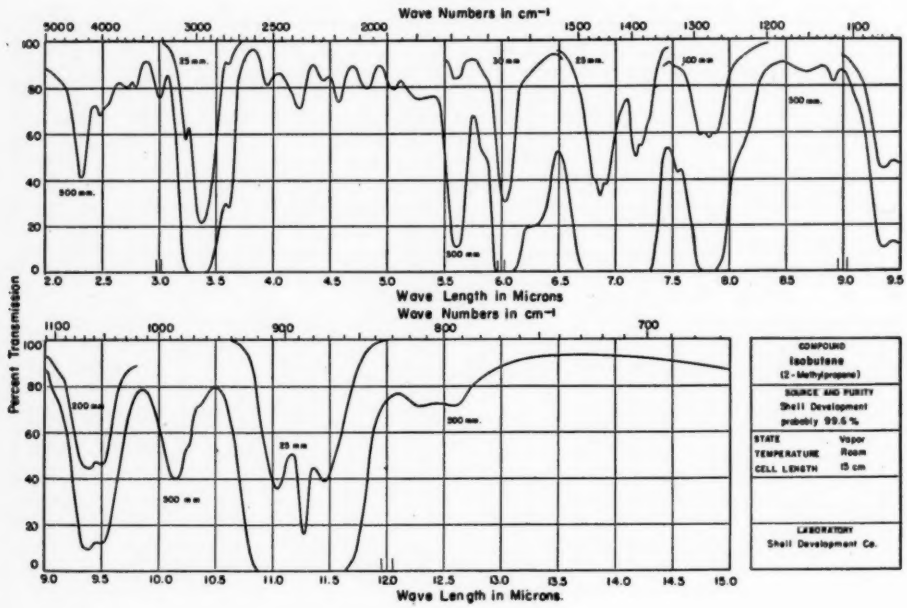


FIG. 6. Infra-red absorption spectrum of isobutene.

3.37$\mu$ (2970 cm$^{-1}$). This 3.2$\mu$ band is not found in the spectra of molecules lacking this group. It undoubtedly represents the antisymmetric CH stretching vibration of the $CH_2$ group, the symmetric one (of lower frequency) being found with all the aliphatic CH stretching frequencies in the strong 2970 cm$^{-1}$ band (or in the case of ethylene as a weak shoulder on the side of the 3120 cm$^{-1}$ band[3]). Frequencies corresponding to the 3.2$\mu$ band are found in the Raman effect at *circa* 3080 cm$^{-1}$.[12]

The region 10 to 12.5$\mu$ shows a feature that is apparently characteristic of olefins in general. All of the compounds discussed here and in the two following articles show either two (in the case of molecules having the $CHR=CH_2$ con-

[12] J. H. Hibben, *The Raman Effect and its Chemical Applications*, A. C. S. Monograph (Reinhold Publishing Corporation, New York, 1939), Chap. 11.

figuration) or one (in the case of other olefins) very strong bands in this region. These bands (or at least the stronger one if there are two) all show 90 percent or more absorption at their maxima for a pressure of 100 mm Hg of olefin in a 15-cm cell. This is stronger absorption by a factor of two or more than the most intense bands of paraffin hydrocarbons. In ethylene this band occurs at 10.5$\mu$, and is known to be caused by the infra-red active out-of-plane bending of the hydrogen atoms. Hence, by analogy, these strong bands in higher olefins may be ascribed to out-of-plane motions of hydrogens attached to the double-bonded carbons. The exact wave-lengths at which these strong bands are found are highly characteristic of the type of substitution around the double bond, as shown in Table III.[13] In the region 5 to 6$\mu$ each of the substances has a fairly strong band which may reasonably be assigned as the first overtone of the strong band at 10 to 12$\mu$, or as a combination with some nearby frequency in the cases where the first overtone is forbidden by symmetry (ethylene, *trans*-2-butene).[14] In the compounds containing the olefinic $CH_2$ group these bands are remarkably intense, whereas in the other molecules they are only slightly stronger than other overtones.

TABLE I. Wave-lengths and frequencies of absorption maxima of ethylene, 12.5–15$\mu$.

| $\lambda(\mu)$ | $\omega(cm^{-1})$ |
|---|---|
| 12.39 | 807.1 |
| 12.535 | 797.7 |
| 12.69 | 788.0 |
| 12.845 | 778.5 |
| 13.01 | 768.6 |
| 13.19 | 758.2 |
| 13.375 | 747.7 |
| 13.54 | 738.6 |
| 13.705 | 729.6 |
| 13.88 | 720.5 |
| 14.10 | 709.2 |
| 14.345 | 697.1 |
| 14.575 | 686.0 |

These three regions, 3$\mu$, 5 to 6$\mu$ and 10 to 12$\mu$, have an important application in the identification of the type of olefin when the complete structure is unknown or uncertain, and have been used in conjunction with other physical and chemical data with considerable success for this purpose.[11,15]

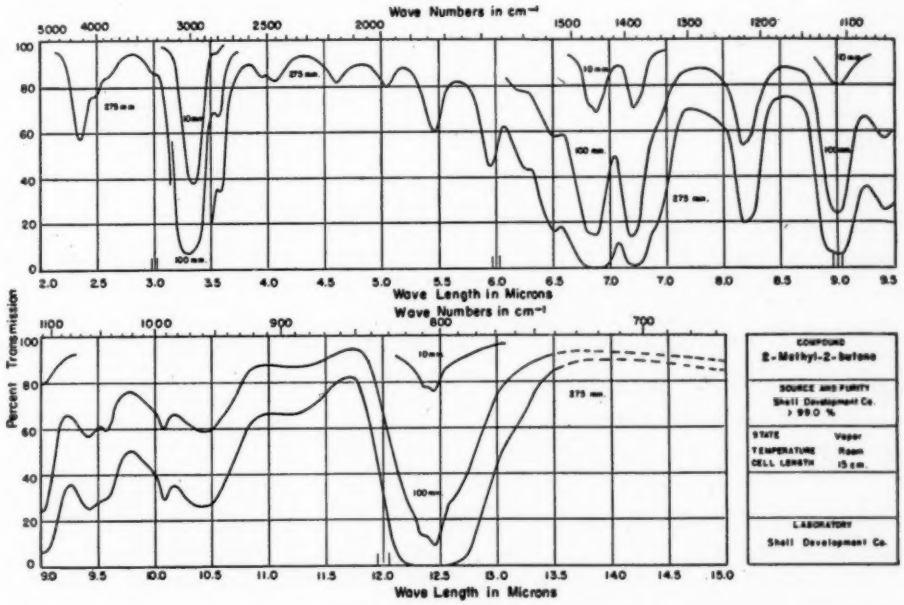


FIG. 7. Infra-red absorption spectrum of 2-methyl-2-butene.

[13] P. Lambert and J. Lecomte, Comptes rendus **206**, 1007 (1938) have enunciated a similar rule regarding strong absorption bands in this region, which was deduced from unpublished spectra of branched and unbranched higher olefins. However, the exact method of application of the rule is not very clear, nor does it seem to apply to the spectra shown here and in the next two articles. This rule has been correctly stated in the recent paper of Thompson and Torkington (reference 11).

[14] This overtone band in 1-butene at 5.43$\mu$ was erroneously interpreted by Barnes *et al.* (reference 6) as being caused by an impurity of 1,3-butadiene.

[15] R. S. Rasmussen, Phys. Rev. **64**, 188 (1943).

TABLE II. Wave-lengths, frequencies, and intensities of absorption maxima (vapor spectra).

| Propylene | | | 1-Butene | | | *cis*-2-Butene | | |
|---|---|---|---|---|---|---|---|---|
| λ(μ) | ω(cm⁻¹) | *I* | λ(μ) | ω(cm⁻¹) | *I* | λ(μ) | ω(cm⁻¹) | *I* |
| 2.11 | 4740 | 0 | 2.12 | 4715 | 0 | 2.30 | 4350 | 1 |
| 2.30 | 4350 | 1 | 2.32 | 4310 | 1 | 2.45 | 4080 | 0, |
| 2.44 | 4100 | 0, | 2.37 | 4220 | 0, | 2.59 | 3860 | 0, |
| 2.58 | 3875 | 0, | *ca.* 2.49 | *ca.* 4015 | 0, | 2.80 | 3570 | 0 |
| 2.77 | 3710 | 0 | 2.73 | 3665 | 0 | 3.01 | 3320 | 0, |
| 2.87 | 3485 | 0 | 3.14 | 3185 | 0, | 3.28 | 3050 | 10 |
| 2.97 | 3365 | 0, | 3.25 | 3075 | 1, | 3.37 | 2965 | |
| 3.22 | 3105 | 2, | 3.365 | 2970 | 10 | 3.61 | 2740 | 0, |
| 3.34 | 2995 | 9 | 3.42 | 2925 | | 3.81 | 2625 | 0 |
| 3.61 | 2770 | 0, | 3.61 | 2770 | 0, | 3.98 | 2515 | 0 |
| 3.75 | 2665 | 0, | 3.82 | 2620 | 0, | 4.22 | 2370 | 1 |
| 3.87 | 2585 | 0 | 4.03 | 2480 | 0 | 4.47 | 2235 | 0, |
| 4.02 | 2485 | 0 | 4.17 | 2400 | 0 | 5.005 | 1998 | 2 |
| 4.18 | 2390 | 0, | 4.42 | 2260 | 0 | 5.16 | 1938 | 0, |
| 4.325 | 2310 | 0 | 4.62 | 2165 | 0 | 5.46 | 1832 | 0 |
| 4.47 | 2235 | 0 | 4.86 | 2060 | 0 | 5.99 | 1669 | 5 |
| *ca.* 4.76 | *ca.* 2100 | 0, | 5.06 | 1976 | 0 | 6.06 | 1650 | |
| 4.89 | 2045 | 1 | 5.46 | 1832 | 4 | 6.17 | 1621 | |
| 4.96 | 2016 | 1 | 6.08 | 1645 | 9 | 6.51 | 1536 | 3, |
| 5.08 | 1969 | 0, | 6.12 | 1634 | | 6.78 | 1475 | 1, |
| 5.44 | 1838 | 3 | 6.45 | 1550 | 1, | 6.905 | 1448 | 8 |
| 5.51 | 1815 | | 6.74 | 1485 | 9 | 7.04 | 1420 | |
| 5.78 | 1730 | 1, | 6.865 | 1457 | | 7.16 | 1397 | |
| 6.03 | 1658 | 8 | 6.98 | 1433 | | 7.27 | 1376 | 1, |
| 6.10 | 1639 | | 7.08 | 1412 | 0, | 8.79 | 1138 | 1 |
| 6.33 | 1580 | 0, | 7.19 | 1391 | 1, | 8.865 | 1128 | |
| 6.45 | 1550 | 0, | 7.54 | 1326 | 3 | 9.44 | 1059 | 4 |
| 6.79 | 1473 | 7 | 7.65 | 1307 | | 9.635 | 1038 | |
| 6.92 | 1445 | | 7.78 | 1285 | | 9.84 | 1016 | |
| 7.16 | 1397 | | 7.91 | 1264 | 0, | 10.14 | 986 | 7 |
| 7.60 | 1316 | | *ca.* 8.11 | *ca.* 1235 | 0, | 10.245 | 976 | |
| 7.70 | 1299 | 0 | 8.40 | 1190 | 1 | 10.335 | 968 | 0 |
| 7.78 | 1285 | | 8.52 | 1174 | | 11.00 | 909 | 1 |
| 8.07 | 1239 | 0, | 8.78 | 1139 | 1, | *ca.* 11.30 | *ca.* 880 | |
| 8.17 | 1224 | 1 | 8.85 | 1130 | | 11.58 | 864 | 0 |
| 8.23 | 1215 | | 8.97 | 1115 | 4 | *ca.* 13.30 | *ca.* 750 | 10 |
| *ca.* 8.39 | *ca.* 1190 | 0 | *ca.* 9.15 | *ca.* 1090 | | 14.86 | 673 | |
| 8.55 | 1170 | | 9.265 | 1079 | | | | |
| 8.64 | 1157 | 1 | 9.98 | 1002 | 9 | | | |
| *ca.* 9.35 | *ca.* 1070 | | 10.07 | 993 | | | | |
| 9.58 | 1044 | 3 | 10.14 | 986 | | | | |
| *ca.* 9.85 | *ca.* 1015 | | 10.82 | 924 | 10 | | | |
| 10.10 | 990 | | 10.965 | 912 | | | | |
| *ca.* 10.55 | *ca.* 950 | 10 | 11.07 | 903 | | | | |
| 10.84 | 923 | | *ca.* 11.57 | *ca.* 864 | 1 | | | |
| 10.95 | 913 | | 11.72 | 853 | | | | |
| 11.25 | 889 | | 11.85 | 844 | | | | |
| 12.98 | 770 | 0 | 12.12 | 825 | 0, | | | |
| 13.41 | 746 | 0 | 12.48 | 801 | 2 | | | |
| 13.54 | 739 | 0 | 12.65 | 791 | | | | |
| 13.68 | 731 | 0 | 12.76 | 784 | | | | |
| 13.85 | 722 | 0 | *ca.* 13.90 | *ca.* 719 | 1, | | | |

In the 6μ region, the C=C stretching frequency is found as expected in all the spectra except those of ethylene and *trans*-2-butene, where it is forbidden by symmetry. The regularities found in this frequency in the Raman effect for various types of substituted ethylenes[12] are followed to some extent in the infra-red, but the shifts are in general so small that the difficulty of fixing the origin of the infra-red bands makes this property of less use in the infra-red spectra of vapors.

Not much regularity can be found in the 7μ (1400 cm⁻¹) region. From the Raman[16] and infra-red[1] spectra of paraffins, it appears that the non-symmetrical HCH bending frequencies of the $CH_3$ group, and the HCH bending frequencies of the $CH_2$ group, are found from 1440 to 1475 cm⁻¹ (6.78 to 6.95μ), and are strong in both the Raman and infra-red. The symmetrical HCH bending frequencies of the $CH_3$ group are found at 1375 to 1395 cm⁻¹ (7.18 to 7.28μ), and are somewhat weaker in the infra-red and either very weak or missing in the Raman effect. As used here, "non-symmetrical" and "symmetrical" refer to the symmetry within the methyl group; that is, to vibrations which in an isolated methyl group (point group $C_{3v}$) would have representations $E$ and $A_1$ respectively. The Raman spectra of olefins containing the $=CH_2$ group show in addition to the above frequencies a fairly strong line at 1415 cm⁻¹, evidently the olefinic HCH bending frequency. The spectra of propylene, 1-butene, isobutene, and 2-methyl-2-butene fit the above picture fairly well, showing the 6.8μ and 7.2μ bands for $CH_3$ and aliphatic

[16] Hibben, reference 9, Chap. 7.

TABLE II.—*Continued.*

| *trans*-2-Butene | | | Isobutene | | | 2-Methyl-2-butene | | |
|---|---|---|---|---|---|---|---|---|
| λ(μ) | ω(cm⁻¹) | *I* | λ(μ) | ω(cm⁻¹) | *I* | λ(μ) | ω(cm⁻¹) | *I* |
| 2.34 | 4275 | 2 | 2.32 | 4310 | 1 | 2.33 | 4290 | 1 |
| 2.47 | 4050 | 0s | 2.49 | 4015 | 0s | 2.47 | 4050 | 0s |
| 2.60 | 3845 | 0 | 2.56 | 3905 | 0s | 2.60 | 3845 | 0s |
| 2.75 | 3635 | 0 | 2.73 | 3665 | 0 | 3.025 | 3305 | 0s |
| 2.94 | 3400 | 0 | 2.80 | 3570 | 0 | 3.38 | 2960 | 9 |
| 3.38 | 2960 | 9 | 3.01 | 3320 | 0 | 3.61 | 2770 | 2s |
| 3.62 | 2760 | 2s | 3.24 | 3085 | 2s | 3.98 | 2515 | 0 |
| 3.83 | 2610 | 0 | 3.37 | 2965 | 1 | 4.10 | 2440 | 0 |
| 3.94 | 2540 | 0s | 3.62 | 2760 | 1s | 4.64 | 2170 | 0 |
| 4.09 | 2445 | 1 | 3.95 | 2530 | 0 | 5.07 | 1972 | 0 |
| 4.22 | 2370 | 0s | 4.23 | 2365 | 1 | 5.475 | 1830 | 1 |
| 4.44 | 2250 | 0 | 4.43 | 2255 | 0 | 5.955 | 1679 | 1 |
| 4.61 | 2170 | 0 | 4.59 | 2180 | 0 | 6.27 | 1595 | 0s |
| 4.79 | 2090 | 0 | 4.83 | 2070 | 0 | 6.50 | 1538 | 1s |
| 5.00 | 2000 | 1 | 5.06 | 1976 | 0 | 6.81 | 1471 | 7 |
| 5.18 | 1931 | 0 | *ca.* 5.28 | *ca.* 1890 | 0 | 6.88 | 1453 | |
| 5.61 | 1783 | 1 | 5.59 | 1789 | 3 | 7.19 | 1391 | 7 |
| 5.89 | 1698 | 2 | 5.65 | 1770 | | 7.26 | 1377 | |
| 6.19 | 1616 | 0s | 5.83 | 1715 | 0s | 7.40 | 1351 | 0s |
| 6.80 | 1471 | 8 | 6.04 | 1656 | 9 | 8.17 | 1224 | 5 |
| 6.90 | 1449 | | *ca.* 6.34 | *ca.* 1575 | 1 | 8.21 | 1218 | |
| 7.02 | 1425 | | 6.81 | 1468 | 10 | 8.25 | 1212 | |
| 7.18 | 1393 | | 6.865 | 1457 | | 8.95 | 1117 | 7 |
| 7.63 | 1311 | 4 | 6.925 | 1444 | | 9.00 | 1111 | |
| 7.73 | 1294 | | 7.185 | 1392 | 9 | 9.04 | 1106 | |
| 7.95 | 1258 | 1 | 7.235 | 1382 | | 9.45 | 1058 | 3 |
| 8.04 | 1244 | | 7.30 | 1370 | 0 | 9.61 | 1041 | |
| 8.32 | 1202 | 1 | 7.55 | 1325 | | 10.12 | 988 | 1 |
| 8.43 | 1186 | | 7.75 | 1290 | 4 | 10.47 | 955 | 3 |
| 9.325 | 1072 | 5 | 7.83 | 1277 | | *ca.* 11.25 | *ca.* 890 | 1 |
| 9.46 | 1057 | | 7.89 | 1271 | 0 | 12.28 | 814 | 9 |
| *ca.* 10.20 | *ca.* 980 | 10 | *ca.* 8.19 | *ca.* 1220 | 0 | 12.37 | 808 | |
| 10.37 | 964 | | 8.68 | 1152 | 0 | 12.47 | 802 | |
| *ca.* 10.62 | *ca.* 940 | 0 | 8.92 | 1121 | 2 | *ca.* 12.7 | *ca.* 790 | 1s |
| *ca.* 13.0 | *ca.* 770 | 0 | 9.37 | 1067 | 1 | *ca.* 13.2 | *ca.* 760 | 0s |
| | | | 9.52 | 1050 | 0s | | | |
| | | | 10.15 | 985 | 0s | | | |
| | | | 10.28 | 973 | | | | |
| | | | 10.37 | 964 | | | | |
| | | | 11.04 | 906 | 10 | | | |
| | | | 11.275 | 887 | | | | |
| | | | 11.46 | 873 | | | | |
| | | | 12.26 | 816 | 0 | | | |
| | | | 12.63 | 792 | 0 | | | |

"*s*" indicates shoulder on an adjacent stronger band.
Some of the weak bands found in the higher pressure runs may be attributable to impurities. In particular the 5.78μ band in propylene (Fig. 2) is explicable as caused by the trace of acrolein present in the sample (see Section II), and weak bands of other compounds in this region may also be due to traces of carbonylic materials.

$CH_2$ groups, but showing little or no indication of the 1415 $cm^{-1}$ frequency of olefinic $CH_2$. Propylene shows none in the present work, but Wilson and Wells,[4] with somewhat better resolution in this region, found a slight bump at 1415 $cm^{-1}$. 1-Butene shows some filling in at this wave-length indicative of a weak band; isobutene shows no indication of a band. The 2-butenes appear to be anomalous in that they show strong absorption around 7.0μ (1430 $cm^{-1}$), where methyl groups in other molecules do not exhibit bands. The inability to resolve the complex of bands in this whole region, and the strong dependence of their relative intensities on structure, make it difficult to deduce any useful or instructive generalizations.

## V. FREQUENCIES AND VIBRATIONAL ASSIGNMENT OF ETHYLENE

The only new feature of the ethylene spectrum is the series of fine structure maxima in the region 12.3 to 14.5μ.[17] The band is weak, as indicated in Fig. 1. Only the series of $P_Q$ maxima were observed, since the long wave-length side of the strong 950 $cm^{-1}$ band overlies the $R_Q$ side. Since this band had never been reported at the time this work was done, the possibility of its being due to an impurity was checked by carrying out a rough distillation in which the first and last quarter fractions were rejected. The middle fraction showed the band with the same intensity. Furthermore, the average spacing between thirteen maxima is 10.1 $cm^{-1}$ (average deviation 0.8 $cm^{-1}$). This spacing is of the correct magnitude for the perpendicular type of band in ethylene.

The lack of a central $Q_Q$ branch shows the band to be of the $B_{2u}$ type (symmetry designation

[17] A preliminary report of this work appears in Phys. Rev. **62**, 301 (1942); Thompson and Harris (reference 10) have given a short discussion of the band.

TABLE III. Strong bands of olefins, 10.0–12.5μ.

| Type | Compounds | Wave-lengths of strong bands (μ) |
|---|---|---|
| $CH_2=CH_2$ | Ethylene | 10.52 |
| $CHR=CH_2$ | Propylene | 10.10, 10.95 |
| | 1-butene | 10.07, 10.965 |
| | 1-pentene | 10.02, 10.94 |
| | 3-methyl-1-butene | 10.01, 10.96 |
| | 1-octene | 10.06, 10.96 |
| | 6-methyl-1-heptene | 10.03, 10.94 |
| | 1,3-butadiene | 9.875, 10.995 |
| | Isoprene* | 10.09, 11.03 |
| | *cis*-1,3-pentadiene* | 10.03, 11.035 |
| | *trans*-1,3-pentadiene* | 9.98, 11.10 |
| CHR=CHR** | *cis*-2-butene | 10.245 |
| | *trans*-2-butene | 10.37 |
| | *trans*-2-pentene *circa* | 10.35 |
| | 2-octene | 10.35 |
| | 3-octene | 10.33 |
| | 4-octene | 10.33 |
| | *cis*-1,3-pentadiene* | 10.37 |
| | *trans*-1,3-pentadiene* | 10.53 |
| $CR_2=CH_2$ | Isobutene | 11.275 |
| | 2-methyl-1-butene | 11.23 |
| | 2-methyl-1-heptene | 11.225 |
| | Isoprene* | 11.20 |
| $CR_2=CHR$*** | 2-methyl-2-butene | 12.47 |

* Isoprene and the pentadienes are each included in two categories.
** Omission of statement of *cis-trans* configuration means that as originally prepared this was not known.
*** Further work on this type of molecule indicates much more variability than for the other types.

of Herzberg[18]), i.e., involves a dipole change along the intermediate axis of inertia. The approximate fixing of the band center by the intensity distribution leads to a value near 800 $cm^{-1}$.

In view of the recent interpretation by Gallaway and Barker[3] of a series of maxima to the short wave-length side of the 950 $cm^{-1}$ band as belonging to the previously unobserved $\nu_9$ fundamental frequency (notation of these authors; Herzberg[18] designates this frequency by $\nu_{10}$), there is some difficulty in assigning the band reported here. On Gallaway and Barker's assignment it cannot be explained as an allowable difference band. The possibility that it is an isotope band ($\nu_{11}$ of the $C^{12}-C^{13}$ molecule) is precluded not only by the lack of a $Q_Q$ branch but also by the fact that, to the harmonic oscillator approximation, the isotopic molecule frequency differs from $\nu_{11}$ of the $C^{12}-C^{12}$ molecule by less than one percent.

It is suggested here that the 800 $cm^{-1}$ band is the $\nu_9$ fundamental. The following discussion represents an exploration of the consequences of such an assumption. Table IV shows the fundamentals using this new assignment. The most reasonable explanation of the 2047 $cm^{-1}$ infra-red band is still $\nu_9+\nu_{10}$, as assumed by Gallaway and Barker, placing the thus-far-unobserved Raman active fundamental $\nu_{10}$ at *circa* 1250 $cm^{-1}$. This allows the rather strong harmonics observed in the infra-red at 4207.9 and 4324.4 $cm^{-1}$ [19] to be interpreted as $\nu_1+\nu_{10}=4240$ $cm^{-1}$, and $\nu_3+\nu_8+\nu_{10}=4317$ $cm^{-1}$, respectively, instead of the fourth harmonic combinations necessitated by Gallaway and Barker's assignment.

Application of the Redlich-Teller product rule and use of the $\nu_9+\nu_{10}$ combination band at 1595 $cm^{-1}$ in the spectrum of $C_2D_4$[3] leads to probable values of 575 and 1020 $cm^{-1}$ for $\nu_9$ and $\nu_{10}$, respectively, in this molecule. This assignment allows the 3204 $cm^{-1}$ band to be interpreted as $\nu_1+\nu_{10}=3220$ $cm^{-1}$ instead of as a fourth harmonic. The band at 3049.0 $cm^{-1}$ in $C_2D_4$ cannot be explained on the assignment proposed here. It seems reasonable, however, that this band may be caused by the C–H stretching vibration of $C_2HD_3$, whose presence was indicated by two other bands. The interpretations offered by Gallaway and Barker for the remainder of the observed harmonic bands in $C_2H_4$ and $C_2D_4$ would not be affected by this new assignment, since they do not involve $\nu_9$ or $\nu_{10}$.

TABLE IV. Fundamental frequencies of $C_2H_4$ and $C_2D_4$.

| | | $C_2H_4$ | $C_2H_4$ |
|---|---|---|---|
| $\nu_1$ | $B_{3u}$ | 2989.5 $cm^{-1}$ | 2200.2 $cm^{-1}$ |
| $\nu_2$ | $A_{1g}$ | 3019.3 | 2251.6 |
| $\nu_3$ | $B_{3u}$ | 1443.9 | 1077.9 |
| $\nu_4$ | $A_{1g}$ | 1342.4 | 981.6 |
| $\nu_5$ | $B_{2u}$ | 3105.5 | 2345 |
| $\nu_6$ | $B_{1g}$ | 3075 | 2306 |
| $\nu_7$ | $A_{1u}$ | (950)* | ? |
| $\nu_8$ | $A_{1g}$ | 1623.3 | 1514.7 |
| $\nu_9$ | $B_{2u}$ | 800* | 575* |
| $\nu_{10}$ | $B_{1g}$ | 1250* | 1020* |
| $\nu_{11}$ | $B_{1u}$ | 949.2 | 720.0 |
| $\nu_{12}$ | $B_{2g}$ | 943 | 780 |

Notation of frequencies same as used by Gallaway and Barker, reference 3. (*) indicates a change from frequency assigned by them.

[18] G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), pp. 325–328.

[19] A. Levin and C. F. Meyer, J. Opt. Soc. Am. **16**, 137 (1928).

Using the new assignment, the specific heat at 300.0°K was calculated to be 10.58 cal./mole degree, in contrast to the experimental value of 10.39 cal./mole degree.[20] The discrepancy is greater by a factor of two or more than the probable experimental error. The high calculated value, arising principally from the two low frequencies $\nu_9$ (800 cm$^{-1}$) and $\nu_7$ (825 cm$^{-1}$), would indicate that $\nu_7$, the torsional frequency, should have a higher value. Indeed, to fit the $C_p$ data, it is necessary to raise $\nu_7$ to *circa* 950 cm$^{-1}$.

It has recently been suggested by Herzberg[18] that the maxima appearing as a band at 800 cm$^{-1}$ arise from the infra-red inactive $A_{1u}$ torsional oscillation ($\nu_7$) made very weakly active by Coriolis interaction with the infra-red active $B_{2u}$ $\nu_9$ vibration (assumed to be at 995 cm$^{-1}$ as assigned by Gallaway and Barker). The inverse of this explanation can also be applied to account for the 995 cm$^{-1}$ band, assuming the 800 cm$^{-1}$ band to be the $\nu_9$ fundamental. This interpretation offers a better assignment of overtones, as detailed above, but it does not offer a ready explanation of the 1656 cm$^{-1}$ Raman line, which is the source of the value 825 cm$^{-1}$ for $\nu_7$ on Gallaway and Barker's assignment. It is apparent that a more detailed theoretical and experimental study will be necessary to decide the matter.

## VI. VIBRATIONAL ASSIGNMENT OF PROPYLENE

The spectrum of propylene (Fig. 2) is in excellent agreement with those of Wilson and Wells[4] and Avery and Ellis.[5] Wilson and Wells used a fluorite prism in the range from 6$\mu$ to 9$\mu$ and consequently succeeded in resolving the 7$\mu$ bands somewhat better than was achieved here. In the region from 9$\mu$ to 14.5$\mu$, however, the instrument used in the present work gave considerably better resolution, so that some further conclusions can be drawn regarding the frequency assignment in this molecule. The strong absorption near 11$\mu$ shows clearly four $Q$-branch-like maxima, at 9.58$\mu$, 10.10$\mu$, 10.84$\mu$, and 10.95$\mu$ (1044, 990, 923 and 913 cm$^{-1}$). The 10.10$\mu$ and 10.95$\mu$ peaks were observed by Avery and Ellis[5] at room temperature. The reality of the weak peak at 10.84$\mu$ is better established than the curve of Fig. 2 indicates, since it has been found also in several other spectra at different pressures. Avery and Ellis[5] show also the spectrum of solid propylene at −195°C, in which there appear bands corresponding to all four of the bands noted above, at wave-lengths 9.59$\mu$, 10.06$\mu$, 10.68$\mu$, and 10.96$\mu$. A series of weak maxima were found in the present work between 13 and 14$\mu$, which were observed by Wilson and Wells as a weak structureless band. The maxima seem to indicate two bands with origins ($Q$ branches) at 12.98$\mu$ and 13.68$\mu$ (770 cm$^{-1}$ and 731 cm$^{-1}$).

TABLE V. Vibrational assignment of propylene, frequencies less than 1300 cm$^{-1}$. (Frequencies in cm$^{-1}$.)

| Infra-red (vapor, this work) | | Raman (liquid, Ananthakrishnan[a]) | Assignment |
|---|---|---|---|
| 7.70$\mu$ | 1299($w$) | 1297($vs$, pol.) | CH in-plane wagging. $P$ and $R$ branches at 1285 and 1316 |
| 8.17 | 1224($w$) | —— | (harmonic or difference) $P$ and $R$ branches at 1215 and 1239 |
| 8.39 | 1190($w$) | —— | (harmonic or difference) |
| 8.55 | 1170($w$) | —— | ($CH_3$ in-plane rocking) $P$ branch at 1157 |
| 9.58 | 1044($m$) | —— | $CH_3$ out-of-plane rocking. Diffuse $P$ and $R$ branches near 1015 and 1070. |
| 10.10 | 990($s$) | —— | CH (or $CH_2$) out-of-plane wagging. Diffuse $P$ and $R$ branches near 950 and 1015 |
| 10.84 | 923($m$) | 920($s$, pol.) | C−C stretching |
| 10.95 | 913($s$) | —— | $CH_2$ (or CH) out-of-plane wagging. Diffuse $P$ and $R$ branches near 890 and 950 |
| 12.98 | 770($vw$) | —— | (difference) |
| 13.68 | 731($vw$) | —— | ($CH_2$ in-plane rocking) $P$ and $R$ branches at 723 and 743 |
| | 578($s$)[b] | 580($w$, $b$, depol.) | $CH_2$ torsion |
| | 417($m$)[b] | 432($m$, pol.) | C=C−C bending |

Assignments in parentheses are uncertain but plausible.
[a] R. Ananthakrishnan, Proc. Ind. Acad. Sci. 3A, 527 (1936).
[b] From Wilson and Wells, reference 4.

In accordance with the discussions given by Wilson and Wells[4] and by Herzberg[21] of the vibrational assignment in propylene, the $CH_3$ and $CH_2$ bending frequencies in the 7$\mu$ (1400 cm$^{-1}$) region, the CH in-plane wagging frequency at 7.70$\mu$ (1299 cm$^{-1}$), the carbon-skeleton bending frequency at 417 cm$^{-1}$ and the torsion about the double bond at 578 cm$^{-1}$ (the latter two found by Wilson and Wells with a KBr prism) are all fairly clear-cut. Thus there remain two $CH_3$ rocking, two $CH_2$ rocking, the out-of-plane CH wagging, and the C−C stretching vibrations to be assigned to the bands between 8$\mu$ and 15$\mu$. There are observed here a complex of bands near 8.5$\mu$, probably consisting of three bands with $Q$

[20] E. J. Burcik, E. H. Eyster, and D. M. Yost, J. Chem. Phys. 9, 118 (1941).

[21] G. Herzberg, reference 18, pp. 354, 355.

branches at 8.17$\mu$, 8.39$\mu$, and 8.55$\mu$ (1224, 1190, and 1170 $cm^{-1}$), and the six bands noted above.

From the discussion given earlier of the strong olefin bands in the 10 to 12$\mu$ region, the strong bands at 10.10$\mu$ and 10.95$\mu$ (990 and 913 $cm^{-1}$) represent the $CH_2$ and CH out-of-plane wagging vibrations. The Raman line at 920 $cm^{-1}$ is to be taken as the C−C stretching frequency from its intensity,[4] and hence is to be correlated with the 10.84$\mu$ (923 $cm^{-1}$) infra-red peak.

From analogy with other molecules and from the normal frequency calculation of Wilson and Wells,[4] the two methyl rocking frequencies are to be expected near 1000 $cm^{-1}$. The peak at 9.58$\mu$ (1044 $cm^{-1}$) is therefore in all probability one of these. The other one and the $CH_2$ in-plane rocking are still uncertain. A plausible guess is that one of the bands near 8.5$\mu$, the 8.55$\mu$ (1170 $cm^{-1}$) band for instance, represents the second methyl rocking frequency, since many methyl-containing compounds exhibit methyl rocking bands near this position. The other two bands in the 8.5$\mu$ region (8.17$\mu$ and 8.39$\mu$) would then have to be explained as harmonic or difference bands. The $CH_2$ in-plane rocking frequency, in accordance with the ethylene assignment postulated above, should be found below 800 $cm^{-1}$, and may be the cause of the very weak 13.68$\mu$ (731 $cm^{-1}$) band. The weak band at 12.98$\mu$ (770 $cm^{-1}$) must be interpreted as a difference band, probably from the low methyl torsion frequency near 200 $cm^{-1}$.

Table V lists this frequency assignment for frequencies less than 1300 $cm^{-1}$.

# Infra-Red Absorption Spectra of Some $C_4$ and $C_5$ Dienes

R. S. RASMUSSEN AND R. ROBERT BRATTAIN
*Shell Development Company, Emeryville, California*

(Received October 28, 1946)

The infra-red absorption spectra from 2 to 15$\mu$ have been obtained of 1,3-butadiene, 1,2-butadiene, isoprene, and *cis*- and *trans*-1,3-pentadiene vapors. Salient features of the spectra are discussed.

## I. INTRODUCTION

THE infra-red absorption spectra are given here for 1,3-butadiene, 1,2-butadiene (methylallene), 2-methyl-1,3-butadiene (isoprene), and *cis*- and *trans*-1,3-pentadiene (piperylene), all in the vapor phase. The spectrum of 1,3-butadiene has been reported previously in the literature,[1] but in general with less resolution than was obtained here.

The spectrograph, experimental details, and accuracy obtained have been discussed in the preceding article,[2] except that the spectrum of *trans*-1,3-pentadiene has been obtained with an absorption path of 70 cm in addition to the previously used path of 15 cm. The sources of the pure materials used are as follows:

*1,3-Butadiene.* The 1,3-butadiene was regenerated from butadiene sulfone. Mass spectrometric analysis indicated not more than 0.2 percent butylene and not more than 0.05 percent butane.

*1,2-Butadiene.* The 1,2-butadiene sample was prepared from crotyl alcohol and distilled in a laboratory column. Its purity is believed to be better than 99 percent as judged from physical constants.

*Isoprene.* Isoprene was regenerated from recrystallized sulfone. Mass spectrometric analysis indicated no amylenes or pentane present, the only impurity being 0.03 percent acetone.

*cis-1,3-Pentadiene.* The sample of *cis*-1,3-pentadiene was obtained through the courtesy of Dr. Craig of the B. F. Goodrich Company, Akron,

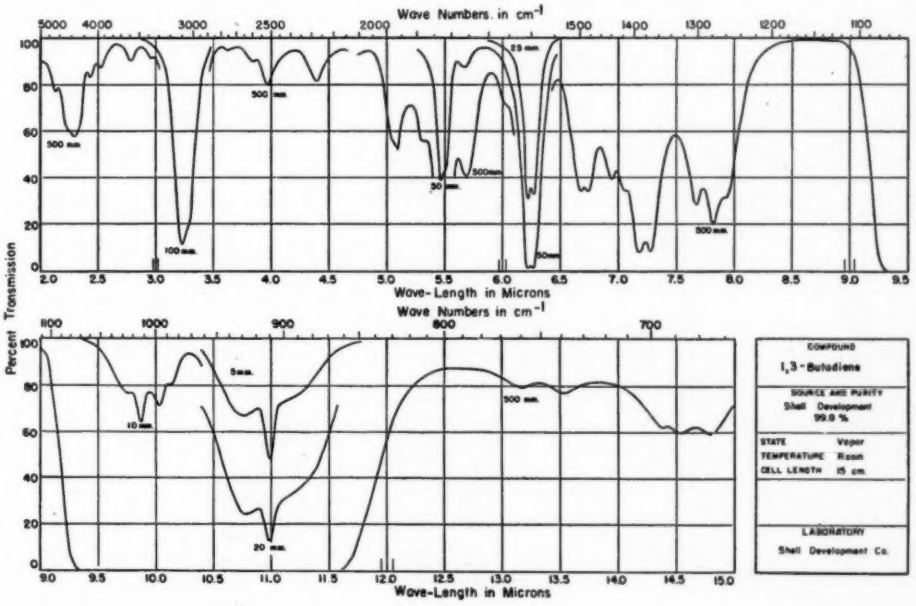


FIG. 1. Infra-red absorption spectrum of 1,3-butadiene.

[1] E. Bartholomé and J. Karweil, Zeits. f. physik. Chemie **35B**, 448 (1937); R. B. Barnes, U. Liddel, and V. Z. Williams, Ind. Eng. Chem., Anal. Ed. **15**, 83 (1943).
[2] R. S. Rasmussen and R. R. Brattain, J. Chem. Phys. **15**, 120 (1947).

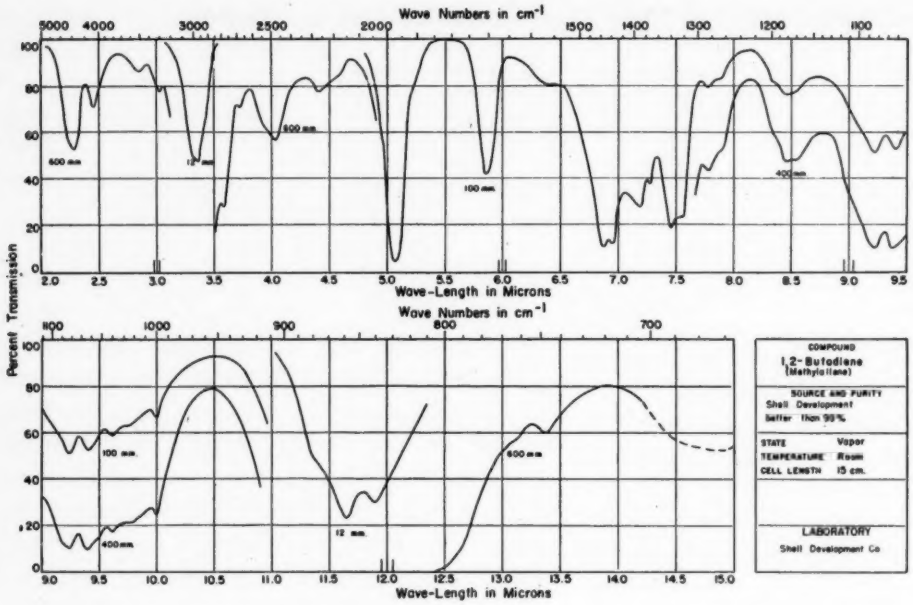


FIG. 2. Infra-red absorption spectrum of 1,2-butadiene.

Ohio.[3] Mass spectrometric analysis indicated no pentane and 0.15 percent amylene. The infra-red spectrum (Fig. 4) shows some indication of the *trans*-isomer by a weak band at 12.2$\mu$, where the

TABLE I. Wave-lengths, frequencies, and intensities of absorption maxima (vapor spectra).

| 1,3-Butadiene | | | Isoprene | | | 1,2-Butadiene | | |
|---|---|---|---|---|---|---|---|---|
| $\lambda(\mu)$ | $\omega(cm^{-1})$ | $I$ | $\lambda(\mu)$ | $\omega(cm^{-1})$ | $I$ | $\lambda(\mu)$ | $\omega(cm^{-1})$ | $I$ |
| 2.13 | 4695 | 0$_s$ | 2.14 | 4675 | 0$_s$ | 2.24 | 4465 | 0$_s$ |
| 2.23 | 4485 | | 2.25 | 4445 | 0$_s$ | 2.29 | 4365 | 1 |
| 2.30 | 4350 | 1 | 2.30 | 4350 | 2 | 2.465 | 4055 | 0 |
| 2.33 | 4290 | | 2.46 | 4065 | 0 | 2.53 | 3955 | 0$_s$ |
| 2.44 | 4100 | 0 | *ca.* 2.59 | *ca.* 3860 | 0$_s$ | 2.85 | 3510 | 0 |
| 2.53 | 3955 | 0 | 3.23 | 3095 | 8 | 3.03 | 3300 | 0$_s$ |
| 2.795 | 3580 | 0 | 3.335 | 3000 | | 3.32 | 3010 | |
| 2.97 | 3365 | 0$_s$ | 3.61 | 2770 | 1$_s$ | 3.37 | 2965 | 9 |
| 3.23 | 3095 | 9 | 3.99 | 2505 | 0 | 3.44 | 2905 | |
| 3.30 | 3030 | | 4.11 | 2435 | 0 | 3.60 | 2775 | 1$_s$ |
| 3.63 | 2755 | 0 | 4.22 | 2370 | 0 | 3.74 | 2675 | 0$_s$ |
| 3.85 | 2595 | 0$_s$ | 4.62 | 2165 | 0 | 3.94 | 2540 | 1 |
| 3.98 | 2515 | 0 | 4.82 | 2075 | 0 | 4.035 | 2480 | |
| 4.41 | 2265 | 0 | 5.065 | 1974 | 1 | 4.42 | 2260 | 0 |
| 4.75 | 2105 | 0 | 5.29 | 1890 | 0 | 4.59 | 2180 | 0$_s$ |
| 5.06 | 1975 | 1 | 5.56 | 1799 | 7 | 5.075 | 1970 | 9 |
| 5.09 | 1965 | | 5.77 | 1733 | 1$_s$ | *ca.* 5.28 | *ca.* 1890 | 1$_s$ |
| 5.31 | 1883 | 0$_s$ | 6.06 | 1650 | 1$_s$ | 5.87 | 1704 | 5 |
| 5.47 | 1828 | 7 | 6.205 | 1612 | 10 | 5.91 | 1692 | |
| 5.50 | 1818 | | 6.24 | 1603 | | *ca.* 6.35 | *ca.* 1570 | 1$_s$ |
| 5.69 | 1757 | 1$_s$ | 6.57 | 1522 | 1 | 6.88 | 1453 | 6 |
| 6.02 | 1661 | 0$_s$ | 6.83 | 1464 | 7 | 6.96 | 1437 | |
| 6.23 | 1605 | 10 | 6.89 | 1451 | | 7.20 | 1389 | 2 |
| 6.275 | 1594 | | 7.04 | 1420 | 4 | 7.29 | 1372 | 1$_s$ |
| 6.68 | 1497 | 1 | 7.20 | 1389 | 7 | 7.46 | 1340 | 6 |
| 6.75 | 1481 | | 7.58 | 1319 | 3 | 7.57 | 1321 | |
| 6.95 | 1439 | 0 | 7.675 | 1303 | | 7.78 | 1285 | 1$_s$ |
| 7.06 | 1416 | 0$_s$ | *ca.* 8.08 | *ca.* 1235 | 0$_s$ | 7.90 | 1266 | |
| 7.195 | 1390 | 5 | *ca.* 8.55 | *ca.* 1170 | 0$_s$ | 8.35 | 1198 | 0$_s$ |
| 7.285 | 1373 | | 8.73 | 1145 | 1 | 8.45 | 1183 | 2 |
| 7.675 | 1303 | | 9.26 | 1080 | | 8.57 | 1167 | |
| 7.82 | 1279 | 3 | 9.33 | 1072 | 5 | *ca.* 9.00 | *ca.* 1110 | |
| 7.98 | 1253 | | 9.41 | 1063 | | 9.235 | 1083 | |
| 9.76 | 1025 | | 9.98 | 1002 | | 9.395 | 1064 | |
| 9.875 | 1013 | 9 | 10.09 | 991 | 9 | 9.48 | 1055 | 4 |
| 10.035 | 997 | | *ca.* 10.22 | *ca.* 980 | | 9.615 | 1040 | |
| 10.135 | 987 | | *ca.* 10.86 | *ca.* 920 | | 9.79 | 1021 | |
| 10.76 | 929 | | 11.03 | 907 | 10 | 9.995 | 1001 | |
| 10.995 | 909 | 10 | 11.20 | 893 | | *ca.* 11.36 | *ca.* 880 | |
| *ca.* 11.30 | *ca.* 885 | | *ca.* 11.90 | *ca.* 840 | | 11.645 | 859 | 10 |
| 13.19 | 758 | 0 | *ca.* 12.08 | *ca.* 825 | 1$_s$ | 11.895 | 841 | |
| 13.54 | 739 | 0 | *ca.* 12.96 | *ca.* 770 | | *ca.* 13.14 | *ca.* 760 | 0$_s$ |
| 14.38 | 695 | | 13.215 | 757 | 3 | 13.75 | 727 | 0$_s$ |
| 14.56 | 687 | 1 | 13.48 | 742 | | *ca.* 14.90 | *ca.* 670 | 1 |
| 14.81 | 675 | | | | | | | |

[3] The preparation and properties are described in J. Am. Chem. Soc. **65**, 1006 (1943).

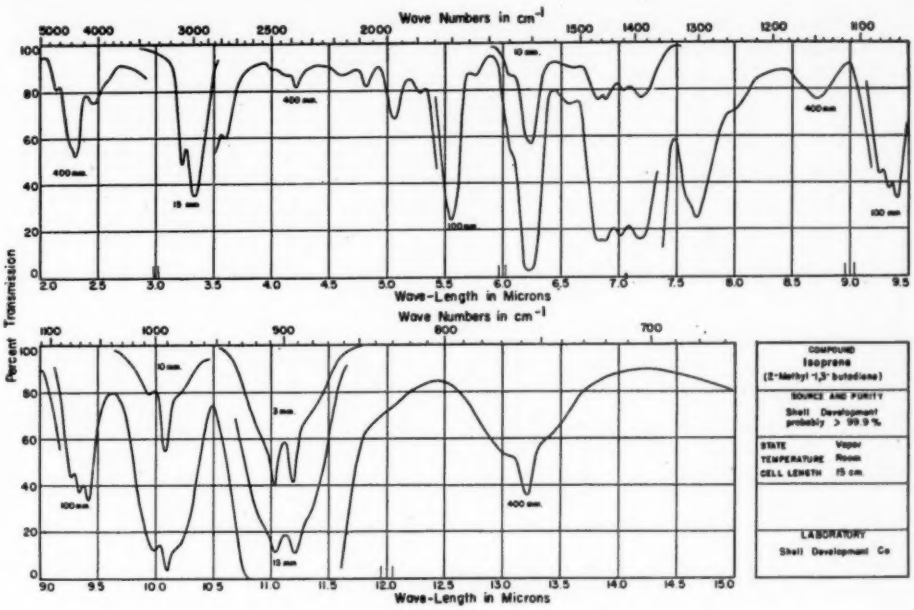


FIG. 3. Infra-red absorption spectrum of isoprene.

TABLE I—*Continued.*

| *cis*-1,3-Pentadiene | | | *trans*-1,3-Pentadiene | | |
|---|---|---|---|---|---|
| λ(μ) | ω(cm⁻¹) | *I* | λ(μ) | ω(cm⁻¹) | *I* |
| 2.12 | 4715 | 0 | 2.33 | 4290 | 1 |
| 2.29 | 4365 | 1 | 3.315 | 3015 | 9 |
| 2.42 | 4130 | 0s | 3.40 | 2940 | |
| 2.57 | 3890 | 0 | 3.64 | 2745 | 1s |
| 2.70 | 3705 | 0 | 3.91 | 2560 | 0 |
| 2.765 | 3615 | 0 | 4.37 | 2290 | 0 |
| 2.92 | 3425 | 0 | 5.00 | 2000 | 0 |
| 3.08 | 3245 | 0s | 5.42 | 1845 | 0s |
| 3.27 | 3060 | 9 | 5.545 | 1803 | 6 |
| 3.36 | 2975 | | 5.67 | 1784 | 0s |
| 3.59 | 2785 | 1s | 6.02 | 1661 | 7 |
| 3.80 | 2630 | 0 | 6.21 | 1610 | 7 |
| 3.92 | 2550 | 1 | 6.51 | 1536 | 1 |
| 4.26 | 2345 | 1 | 6.56 | 1524 | |
| 4.39 | 2280 | 0s | 6.88 | 1453 | 7 |
| 4.67 | 2140 | 0 | 7.03 | 1422 | |
| 5.02 | 1992 | 1 | 7.22 | 1385 | 0s |
| 5.13 | 1949 | 0 | 7.60 | 1316 | 3 |
| 5.22 | 1916 | 0s | 7.70 | 1299 | |
| 5.36 | 1866 | 0s | 7.81 | 1280 | |
| 5.50 | 1818 | 6 | 7.91 | 1266 | 0s |
| 5.645 | 1771 | 1 | 8.17 | 1224 | 2 |
| 5.77 | 1733 | 1 | 8.50 | 1166 | 2 |
| 6.04 | 1656 | 6 | 9.83 | 1017 | 9 |
| 6.22 | 1608 | 7 | 9.98 | 1002 | |
| 6.26 | 1597 | | 10.15 | 985 | |
| 6.56 | 1524 | 1 | 10.54 | 949 | 1 |
| 6.80 | 1471 | 1s | 10.97 | 912 | 9 |
| 6.92 | 1445 | 8 | 11.12 | 899 | |
| 6.97 | 1435 | | 11.32 | 883 | |
| 7.19 | 1391 | 4 | 12.02 | 832 | |
| 7.645 | 1308 | 2 | 12.195 | 820 | 5 |
| 7.735 | 1293 | | 12.41 | 806 | |
| 7.94 | 1259 | 3 | | | |
| 8.00 | 1250 | | | | |
| 8.52 | 1174 | 1 | | | |
| 8.60 | 1163 | | | | |
| 8.85 | 1130 | 2 | | | |
| 8.935 | 1119 | | | | |
| 9.91 | 1009 | 8 | | | |
| 10.03 | 997 | | | | |
| 10.37 | 964 | | | | |
| 10.52 | 951 | | | | |
| 10.86 | 921 | | | | |
| 11.035 | 906 | 10 | | | |
| 11.22 | 891 | | | | |
| 12.22 | 818 | 0s | | | |
| 12.73 | 786 | 6 | | | |
| 12.93 | 773 | | | | |
| 13.20 | 758 | | | | |
| 14.33 | 698 | 0 | | | |

"*s*" indicates shoulder on an adjacent stronger band.

*trans*-isomer has a strong band. If one assumes this explanation of the 12.2μ band, the sample contains about 3 percent of *trans*-1,3-pentadiene.

*trans-1,3-Pentadiene.* The sample of *trans*-1,3-pentadiene was obtained by regeneration from the recrystallized sulfone. Mass spectrometric analysis showed no pentane and 0.15 percent amylene. The infra-red spectrum (Fig. 5) contains no detectable band at 12.9μ, where *cis*-1,3-pentadiene has a strong band. From this the *cis*-content is estimated to be less than one percent.

The spectra are shown in Figs. 1 to 5, and the wave-lengths and frequencies of bands are given in Table I.

## II. DISCUSSION

The general features of the spectra of olefins discussed in the preceding paper[2] are for the most part found as expected in the diene spectra. In the 3μ region, 1,3-butadiene and isoprene show the band at 3.2μ due to the olefinic $CH_2$ group. However, 1,2-butadiene and the 1,3-pentadienes show bands at 3.3 to 3.4μ, with no marked shoulder at 3.2μ.

In the 7μ region (HCH bending vibrations), 1,2-butadiene, isoprene, and the 1,3-pentadienes have bands at both 6.8μ and 7.2μ as would be expected of molecules containing methyl groups. Only a single strong band in this region, at 7.2μ, is shown by 1,3-butadiene.

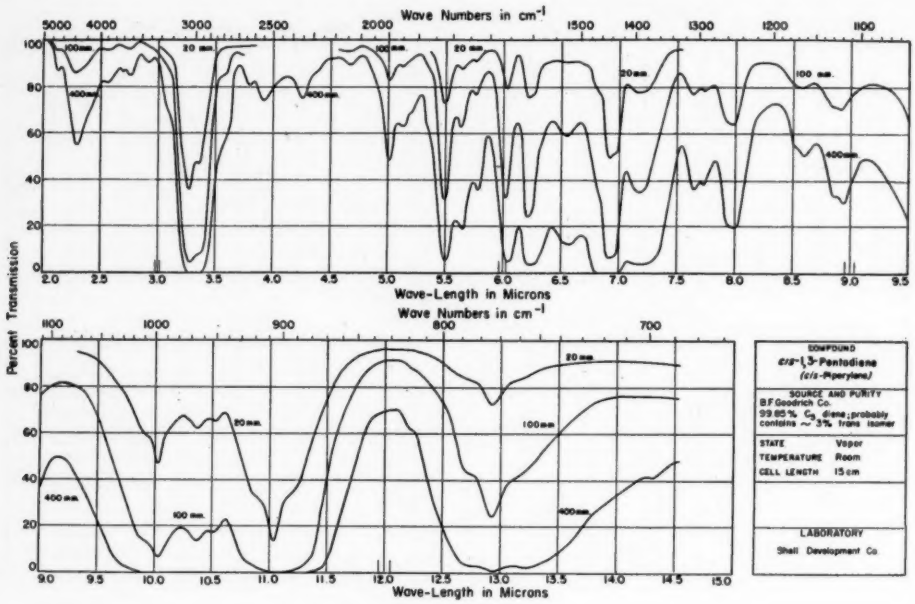


FIG. 4. Infra-red absorption spectrum of *cis*-1,3-pentadiene.

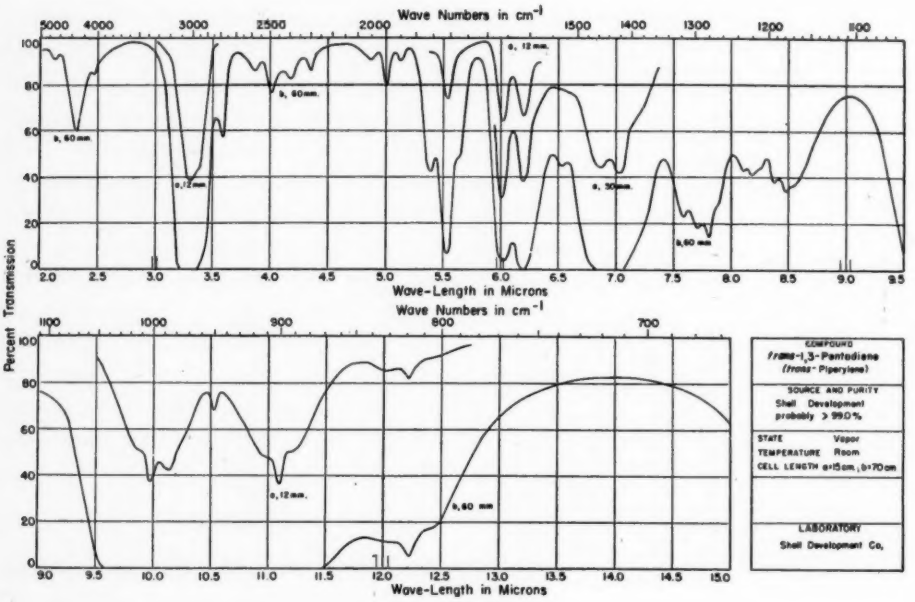


FIG. 5. Infra-red absorption spectrum of *trans*-1,3-pentadiene.

The very strong absorptions in the 10 to 12$\mu$ region agree well with the regularities noted in the mono-olefin spectra (see Table III, preceding paper[2]). An exception is 1,2-butadiene, which has only a single strong band at 11.6$\mu$. It would, however, not be expected that allene-type compounds fit such a scheme, since the forces governing out-of-plane bending of the hydrogen atoms would be different from those in an isolated double bond. What are very probably the first overtones of the strong 10 to 12$\mu$ bands are found as moderately strong bands in the 5.5 to 5.8$\mu$ region.

In the 6$\mu$ region, 1,3-butadiene has a single strong band at 6.24$\mu$ (1603 cm$^{-1}$). Since at room temperature this compound supposedly consists predominantly of the *trans*-form,[4] this is the only C=C stretching frequency which should be observed. It is possible that the very weak band at 6.02$\mu$ (1661 cm$^{-1}$) is due to one of the C=C

[4] R. S. Mulliken, Rev. Mod. Phys. **14**, 265 (1942).

stretching frequencies of the smaller amount of *cis*-form present.[5] Isoprene also shows, surprisingly, only one strong band in this region, at 6.24$\mu$ (1603 cm$^{-1}$). In this case, where there are no symmetry selection rules operating, two bands would be expected for the two C=C stretching frequencies. Both *cis*- and *trans*-1,3-pentadiene are normal in this respect, each showing two moderately strong bands, at 6.03$\mu$ and 6.23$\mu$ (1658 and 1605 cm$^{-1}$).

The C=C stretching frequencies of 1,2-butadiene, like those of allene, would be expected to be widely separated from the normal C=C frequency region (*ca.* 1650 cm$^{-1}$) because of the large amount of mechanical resonance. By analogy with the well-understood allene spectrum[6] they appear as the bands at 5.075$\mu$ and 9.395$\mu$ (1970 and 1064 cm$^{-1}$).

Further interpretation of these spectra will not be attempted in view of the relative complexity of the molecules and the lack of good understanding of hydrocarbon spectra in general.

The authors gratefully acknowledge the assistance of Messrs. D. H. Merrill and P. S. Zucco and of Mrs. Z. Alcorn and Miss L. Bassi in the operation of the spectrograph and in calculation and drawing of curves for this and the preceding paper.

[5] R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, J. Chem. Phys. 11, 432 (1943).

[6] J. W. Linnett and W. H. Avery, J. Chem. Phys. 6, 686 (1938).

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# Infra-Red Absorption Spectra of Some Octenes

R. S. Rasmussen, R. Robert Brattain, and P. S. Zucco
*Shell Development Company, Emeryville, California*

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The infra-red absorption spectra in the 2$\mu$ to 15$\mu$ region of 1-octene, 2-octene, 3-octene, 4-octene, 2-methyl-1-heptene, 6-methyl-1-heptene, and 2,4,4-trimethyl-1-pentene are given. Salient features of the spectra are discussed.

## I. INTRODUCTION

IN continuation of the study of the absorption spectra of olefins commenced in the two preceding articles,[1] results are given here on the spectra of seven octenes. The normal octenes and methylheptenes were pure hydrocarbons obtained from the American Petroleum Institute, and were prepared under the direction of Professor C. C. Boord of the Department of Chemistry of the Ohio State University as part of the American Petroleum Institute Hydrocarbon Research Project in the Industrial Research Foundation of the University. The 2,4,4-trimethyl-1-pentene was prepared at the Shell Development Company Laboratories by repeated careful distillation from a sample of commercial di-isobutylene. Its final purity, as determined from physical constants, is believed to be better than 99.5 percent. *Cis*- and *trans*-configurations are discussed in footnote 6.

The spectrograph, experimental details, and accuracy for the vapor spectra were discussed in the first article of this series.[1] However, a change in wave-length calibration was noted during the runs reported in the present paper. This was corrected as well as possible, but there were not sufficient quantities of samples to rerun the spectra and insure the accuracy claimed for the previous work. Hence the limits of error of wavelengths are estimated to be about $\pm 0.03\mu$ for the spectra of the octenes. Because of the low vapor pressure of the octenes an absorption path of 58 cm was used in obtaining the vapor spectra. For the liquid spectra, cells were used whose design was a modification of the type described

[1] R. S. Rasmussen and R. R. Brattain, J. Chem. Phys. 15, 120, 131 (1947).

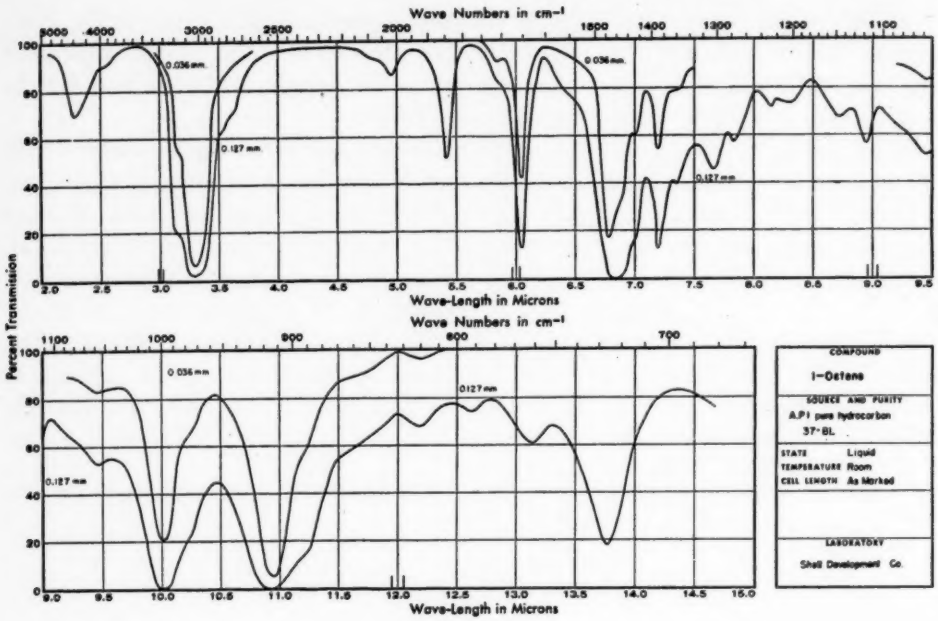


FIG. 1. Infra-red absorption spectrum of 1-octene.

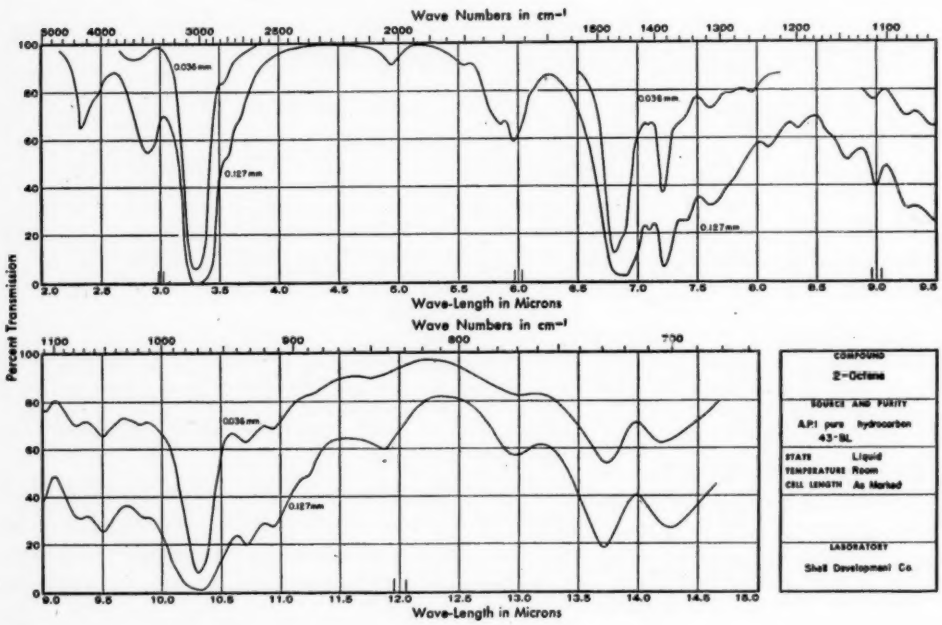


FIG. 2. Infra-red absorption spectrum of 2-octene.

by Gildart and Wright.[2] The cell thicknesses are shown on the individual curves and are probably accurate to about 10 percent. Whereas in the vapor spectra transmission values were obtained by measuring the radiation through the same cell empty and filled, the difficulty of repeatedly emptying and filling the liquid cell necessitated the use of another technique. A block of salt of the same thickness as the sum of the two windows of the liquid cell was put in the light beam to get a measure of the energy transmitted by the empty cell. The ratio of the deflection produced through the filled cell to the deflection through this rocksalt blank was taken as the transmission. A solid block was used instead of

[2] L. Gildart and N. Wright, Rev. Sci. Inst. **12**, 204 (1941). The modification will be described in a forthcoming note by B. M. Burchard and R. R. Brattain.

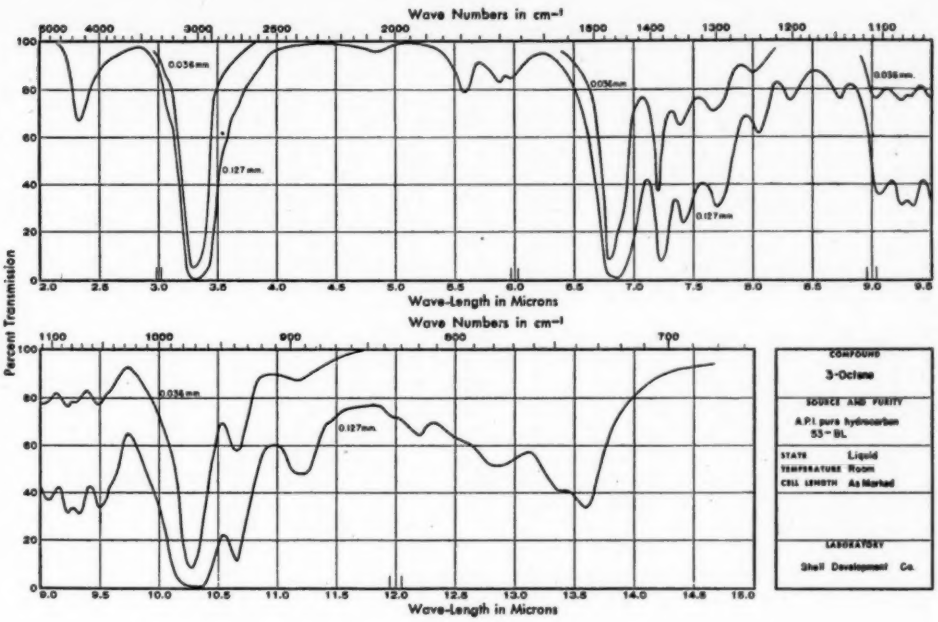
Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1800 1600 1400 1300 1200 1100
0.036 mm
0.127 mm
Percent Transmission
Wave-Length in Microns
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Numbers in cm⁻¹
1100 1000 900 800 700
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave-Length in Microns
COMPOUND
3-Octene
SOURCE AND PURITY
A.P.I. pure hydrocarbon
53-BL
STATE Liquid
TEMPERATURE Room
CELL LENGTH As Marked
LABORATORY
Shell Development Co.

FIG. 3. Infra-red absorption spectrum of 3-octene.

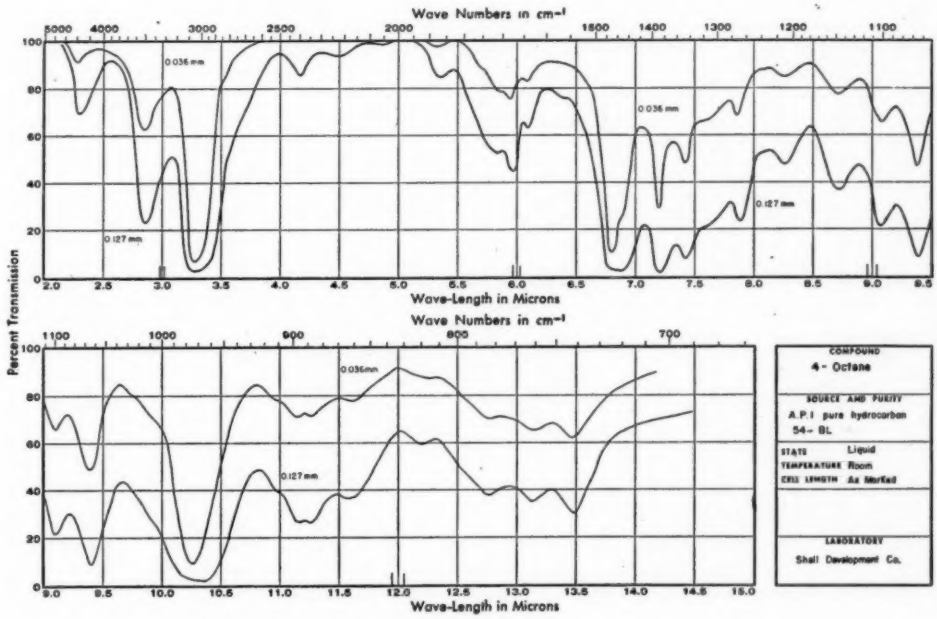
Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1800 1600 1400 1300 1200 1100
0.036 mm
0.127 mm
Percent Transmission
Wave-Length in Microns
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Numbers in cm⁻¹
1100 1000 900 800 700
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave-Length in Microns
COMPOUND
4-Octene
SOURCE AND PURITY
A.P.I. pure hydrocarbon
54-BL
STATE Liquid
TEMPERATURE Room
CELL LENGTH As Marked
LABORATORY
Shell Development Co.

FIG. 4. Infra-red absorption spectrum of 4-octene.

an empty duplicate cell because the former approximates more closely, as far as reflection losses go, to the ideal comparison cell which would contain a non-absorbing material of the same refractive index as the material being studied. However, since it is impossible with the block to duplicate exactly losses due to reflection, scattering, and absorption by cell windows, the errors in the transmission values are accordingly increased considerably above those for the vapor curves, although they are believed to be no more than 10 percent in any case.

## II. RESULTS

The spectra of the liquids are shown in Figs. 1 to 7. Spectra of the vapors are not shown, since they are so similar to the liquid spectra as to make this unnecessary. Table I lists the wavelengths and intensities of absorption maxima for both liquid and vapor. Since the vapor

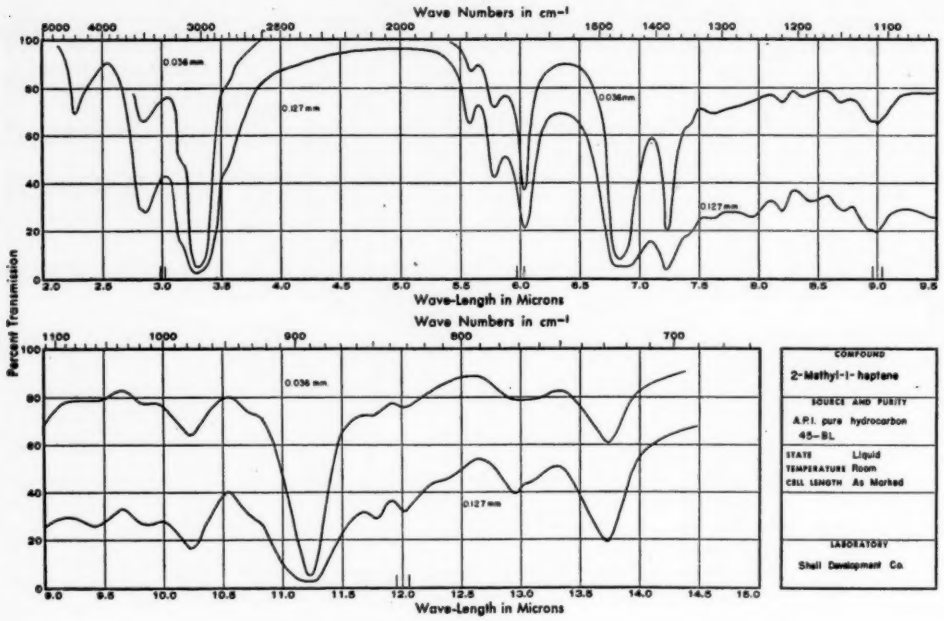
Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1800 1600 1400 1300 1200 1100
0.036 mm
0.127 mm
Percent Transmission
Wave-Length in Microns
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Numbers in cm⁻¹
1100 1000 900 800 700
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave-Length in Microns
COMPOUND
2-Methyl-1-heptene
SOURCE AND PURITY
A.P.I. pure hydrocarbon
45-BL
STATE Liquid
TEMPERATURE Room
CELL LENGTH As Marked
LABORATORY
Shell Development Co.

FIG. 5. Infra-red absorption spectrum of 2-methyl-1-heptene.

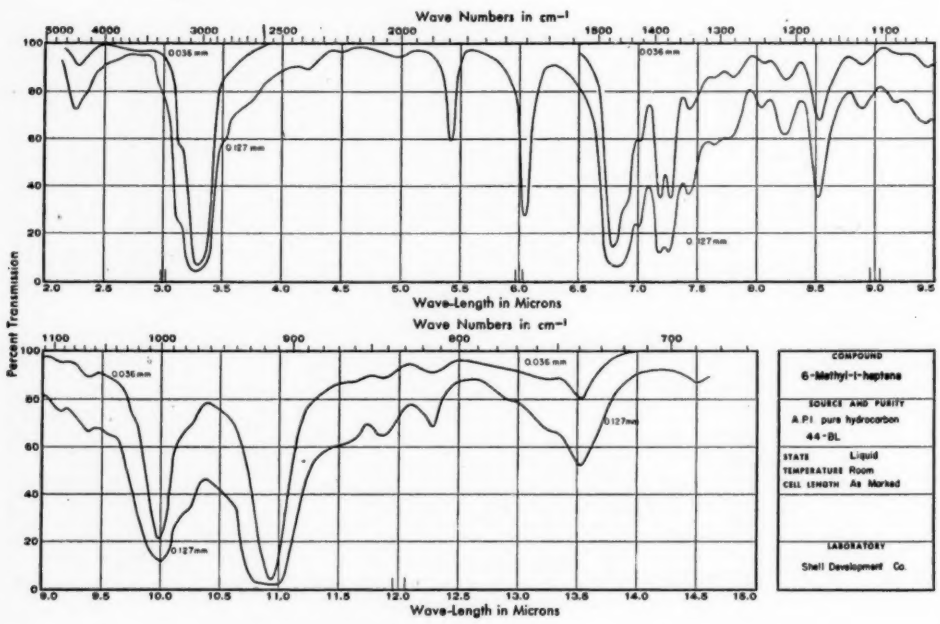
Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1800 1600 1400 1300 1200 1100
0.036 mm
0.127 mm
Percent Transmission
Wave-Length in Microns
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Numbers in cm⁻¹
1100 1000 900 800 700
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave-Length in Microns
COMPOUND
6-Methyl-1-heptene
SOURCE AND PURITY
A.P.I. pure hydrocarbon
44-BL
STATE Liquid
TEMPERATURE Room
CELL LENGTH As Marked
LABORATORY
Shell Development Co.

FIG. 6. Infra-red absorption spectrum of 6-methyl-1-heptene.

pressure is low, many of the weaker bands found in the liquid runs were not observed in the vapor. The spectrum of 1-octene vapor has been published previously by Kettering and Sleator,[3] and the present work agrees well with this. The same article also shows a spectrum of di-isobutylene vapor which closely resembles the spectrum of liquid 2,4,4-trimethyl-1-pentene shown here, with some differences due probably to the difference in state.

Raman spectra of 1-octene, 2-octene, 3-octene, 4-octene, 2-methyl-1-heptene, and 6-methyl-1-heptene have been reported by Cleveland,[4] and of 2,4,4-trimethyl-1-pentene by Rank and Bordner.[5] There are a remarkably large number of

[3] C. F. Kettering and W. W. Sleator, Physics **4**, 39 (1933).

[4] F. F. Cleveland, J. Chem. Phys. **11**, 1 (1943); Phys. Rev. **63**, 224 (1943).

[5] D. H. Rank and E. R. Bordner, J. Chem. Phys. **3**, 248 (1935).

TABLE I. Wave-lengths and intensities of absorption maxima.

| 1-Octene (vapor) | | 1-Octene (liquid) | | 2-Octene (vapor) | | 2-Octene (liquid) | |
|---|---|---|---|---|---|---|---|
| λ(μ) | I | λ(μ) | I | λ(μ) | I | λ(μ) | I |
| 2.305 | 1 | 2.28 | 3 | 3.365 | 10 | 2.30 | 3 |
| 3.25 | 1s | 2.55 | 0s | 3.46 | 0s | 2.445 | 0s |
| 3.39 | 9 | 3.23 | 1s | 3.58 | 0s | 2.925 | 3 |
| 3.45 | 0s | 3.37 | 9 | 5.85 | 1 | 3.36 | 10 |
| 5.47 | 2 | 3.59 | 0s | 6.82 | 8 | 3.58 | 1s |
| 6.065 | 6 | 3.69 | 1s | 7.20 | 5 | 3.70 | 0s |
| 6.82 | 7 | 4.835 | 0s | 7.38 | 1s | 4.97 | 1 |
| 7.03 | 1s | 5.00 | 1 | 7.60 | 3 | 5.57 | 0s |
| 7.20 | 4 | 5.46 | 5 | 7.78 | 0s | 5.815 | 1s |
| 7.34 | 1s | 5.89 | 0s | 8.10 | 1 | 5.89 | 2 |
| 7.66 | 2 | 6.085 | 9 | 8.32 | 0 | 6.00 | 3 |
| 7.84 | 1 | 6.42 | 1s | 8.99 | 1 | 6.15 | 0s |
| 9.515 | 1 | 6.83 } | 10 | 9.25 | 1 | 6.85 } | 10 |
| 10.06 | 7 | 6.935 } | | 9.525 | 2 | 6.915 } | |
| 10.96 | 9 | 7.055 | 3s | 10.35 | 9 | 7.13 | 3 |
| 13.75 | 2 | 7.24 | 8 | 13.71 | 3 | 7.255 | 8 |
| 14.62 | 1 | 7.39 | 2s | 14.36 | 3 | 7.45 | 2s |
| | | 7.70 | 4 | | | 7.65 | 5 |
| | | 7.865 | 3 | | | 8.12 | 2 |
| | | 8.17 } | 2 | | | 8.36 | 2 |
| | | 8.34 } | | | | 8.60 | 0s |
| | | 8.75 | 2 | | | 8.78 | 3 |
| | | 8.975 | 4 | | | 9.03 | 4 |
| | | 9.26 | 0s | | | 9.29 } | 4 |
| | | 9.495 | 2 | | | 9.54 } | |
| | | 10.07 | 10 | | | 9.77 | 0s |
| | | 10.31 | 2s | | | 9.87 | 1s |
| | | 10.99 | 10 | | | 10.35 | 10 |
| | | 11.275 | 2s | | | 10.745 | 5s |
| | | 11.74 | 0s | | | 11.005 | 4s |
| | | 12.14 } | 2 | | | 11.265 | 1s |
| | | 12.24 } | | | | 11.89 | 3 |
| | | 12.66 | 2 | | | 13.03 | 3s |
| | | 13.18 | 3 | | | 13.76 | 6 |
| | | 13.80 | 8 | | | 14.26 | 6 |

| 3-Octene (vapor) | | 3-Octene (liquid) | | 4-Octene (vapor) | | 4-Octene (liquid) | |
|---|---|---|---|---|---|---|---|
| λ(μ) | I | λ(μ) | I | λ(μ) | I | λ(μ) | I |
| 2.305 | 1 | 2.31 | 3 | 2.26 | 1 | 2.25 | 3 |
| 3.375 | 10 | 3.12 | 0s | 3.37 | 10 | 2.865 | 8 |
| 3.43 | 0s | 3.34 | 10 | 3.47 | 0s | 3.33 | 10 |
| 5.58 | 1 | 3.63 | 0s | 5.39 | 1 | 3.60 | 0s |
| 6.02 | 1 | 3.73 | 0s | 5.78 | 1 | 4.215 | 1 |
| 6.81 | 7 | 3.85 | 0s | 6.79 } | 7 | 4.52 | 1 |
| 7.20 | 4 | 4.905 | 0 | 6.84 } | | 4.90 | 0 |
| 7.40 | 3 | 5.61 | 2 | 7.195 | 5 | 5.37 | 2 |
| 7.69 | 3 | 5.89 } | 2 | 7.41 | 4 | 5.73 | 0s |
| 8.02 | 1 | 6.00 } | | 7.64 | 2 | 5.85 | 1s |
| 9.06 | 2 | 6.82 | 10 | 7.88 | 3 | 5.98 | 6 |
| 9.29 | 2 | 6.895 | 0s | 9.07 | 3 | 6.11 | 1s |
| 9.545 | 2 | 6.925 | 0s | 9.41 | 4 | 6.42 | 3 |
| 10.33 | 8 | 7.25 | 9 | 10.33 | 9 | 6.84 | 10 |
| 10.73 | 1s | 7.44 | 8 | 11.225 | 2 | 6.94 | 1s |
| 10.89 | 0s | 7.705 | 7 | 13.01 | 2 | 7.235 | 10 |
| 13.06 | 1 | 8.04 | 4 | | | 7.445 | 9 |
| 13.51 | 2 | 8.32 | 2 | | | 7.645 | 8 |
| | | 8.74 | 2 | | | 7.885 | 8 |
| | | 9.07 } | | | | 8.255 | 5 |
| | | 9.27 } | 7 | | | 8.73 | 6 |
| | | 9.35 } | | | | 9.11 | 8 |
| | | 9.55 } | | | | 9.42 | 9 |
| | | 9.67 | 0s | | | 9.565 | 0s |
| | | 10.33 | 10 | | | 9.79 | 0s |
| | | 10.725 | 9 | | | 9.95 | 0s |
| | | 11.225 | 5 | | | 10.29 | 10 |
| | | 11.535 | 0s | | | 10.99 | 0s |
| | | 11.99 | 0s | | | 11.175 } | 7 |
| | | 12.25 | 4 | | | 11.285 } | |
| | | 12.56 | 0s | | | 11.62 | 6 |
| | | 12.89 | 5 | | | 12.18 | 4 |
| | | 13.42 | 1s | | | 12.57 | 0s |
| | | 13.565 | 7 | | | 12.77 | 6 |
| | | | | | | 13.15 | 7 |
| | | | | | | 13.49 | 7 |

TABLE I.—*Continued.*

| 2-Methyl-1-heptene (vapor) | | 2-Methyl-1-heptene (liquid) | | 6-Methyl-1-heptene (vapor) | | 6-Methyl-1-heptene (liquid) | |
|---|---|---|---|---|---|---|---|
| λ(μ) | I | λ(μ) | I | λ(μ) | I | λ(μ) | I |
| 2.315 | 1 | 2.22 | 3 | 2.28 | 1 | 2.235 | 2 |
| 3.23 | 0s | 2.855 | 7 | 2.66 | 1 | 2.355 | 1s |
| 3.365 | 10 | 3.17 | 1s | 3.22 | 1s | 2.83 | 0 |
| 3.44 | 0s | 3.33 | 10 | 3.37 | 10 | 3.025 | 0s |
| 3.62 | 0s | 3.60 | 1s | 3.45 | 0s | 3.20 | 2s |
| 5.59 | 2 | 5.59 | 4 | 3.64 | 0s | 3.36 | 10 |
| 6.04 | 6 | 5.79 | 6 | 5.43 | 2 | 3.59 | 1s |
| 6.82 | 8 | 6.04 | 8 | 6.045 | 6 | 3.79 | 0s |
| 7.205 | 6 | 6.85 | 10 | 6.78 | 7 | 4.285 | 1 |
| 7.40 | 1s | 7.245 | 10 | 7.21 | 6 | 4.555 | 0 |
| 7.68 } | 2 | 7.42 | 0s | 7.41 | 1s | 4.99 | 1 |
| 7.86 } | | 7.605 | 7 | 7.81 | 1 | 5.45 | 4 |
| 8.97 | 2 | 7.915 | 7 | 8.51 | 3 | 6.065 | 7 |
| 10.34 | 3 | 8.18 | 7 | 8.88 | 1 | 6.81 } | 10 |
| 11.225 | 9 | 8.38 | 7 | 10.03 | 6 | 6.945 } | |
| 11.92 | 2 | 8.675 | 7 | 10.94 | 9 | 7.035 | 5s |
| 13.06 | 2 | 8.91 } | 8 | 11.58 | 0s | 7.21 } | 7 |
| 13.67 | 2 | 8.985 } | | 13.57 | 1 | 7.29 } | |
| | | 9.48 | 7 | | | 7.45 | 3s |
| | | 9.90 | 7 | | | 7.66 } | 3s |
| | | 10.30 | 8 | | | 7.795 } | |
| | | 10.81 | 0s | | | 8.04 | 2 |
| | | 11.275 | 10 | | | 8.24 | 3 |
| | | 11.825 | 7 | | | 8.52 | 6 |
| | | 12.05 | 7 | | | 8.89 | 2 |
| | | 12.35 | 0s | | | 9.185 | 2 |
| | | 12.99 | 6 | | | 9.445 | 2 |
| | | 13.10 | 0s | | | 9.62 | 1s |
| | | 13.755 | 8 | | | 9.81 | 0s |
| | | | | | | 10.05 | 9 |
| | | | | | | 10.31 | 2s |
| | | | | | | 10.565 | 0s |
| | | | | | | 10.975 | 10 |
| | | | | | | 11.64 | 1s |
| | | | | | | 11.90 | 2 |
| | | | | | | 12.33 | 2 |
| | | | | | | 12.96 | 1s |
| | | | | | | 13.32 | 1s |
| | | | | | | 13.555 | 4 |
| | | | | | | 14.53 | 1 |

2,4,4-Trimethyl-1-pentene (liquid)

| λ(μ) | I | λ(μ) | I | λ(μ) | I | λ(μ) | I |
|---|---|---|---|---|---|---|---|
| 2.315 | 3 | 4.32 | 0 | 6.765 } | 10 | 8.905 | 0 |
| 2.42 | 0s | 4.51 | 0 | 6.83 } | | 9.32 | 1 |
| 2.56 | 0s | 4.665 | 0 | 6.94 } | | 9.57 | 3 |
| 3.00 | 0s | 4.84 | 0 | 7.19 } | 10 | 9.77 | 0 |
| 3.13 | 0s | 5.22 | 0 | 7.29 } | | 10.01 | 3 |
| 3.27 | 0s | 5.37 | 0 | 7.33 } | | 10.18 | 1 |
| 3.39 } | 10 | 5.60 | 4 | 7.55 | 4 | 10.30 | 0 |
| 3.44 } | | 5.76 | 1 | 7.74 | 1 | 10.75 | 1s |
| 3.625 | 1s | 6.08 | 8 | 7.92 | 4 | 11.195 | 10 |
| 3.77 | 1s | 6.36 | 0 | 8.08 | 6 | 12.10 | 5 |
| 4.15 | 0 | | | 8.32 | 5 | 13.07 | 7 |
| | | | | 8.67 | 2 | | |

"s" indicates shoulder on an adjacent stronger band.

good coincidences between the Raman and infra-red frequencies in the liquid, but the significance of this is not great in view of the present lack of clear understanding of the spectra of large molecules.

## III. DISCUSSION

The regularities discussed in the first paper of this series[1] are brought out very clearly here:

*1.* In the 3μ region, the absorptions due to $=CH_2$ groups in 1-octene, 2-methyl-1-heptene, and 6-methyl-1-heptene appear as shoulders at 3.2μ. The other compounds show simply the strong 3.35μ band.

*2.* In the 10 to 12μ region, strong bands are

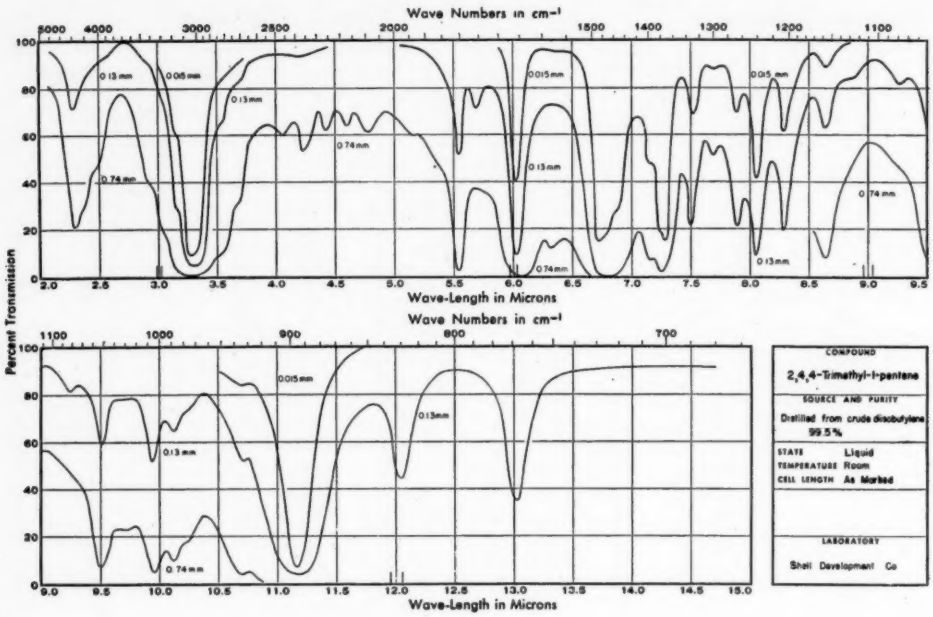


FIG. 7. Infra-red absorption spectrum of 2,4,4,-trimethyl-1-pentene.

found at positions characteristic of the type of substitution around the C=C bond[6] (see Table III in the first paper[1]).

*3.* In the 5 to 6$\mu$ region, bands are found which are very probably overtones of the strong 10 to 12$\mu$ bands.

An additional feature is noticed in these curves. Those molecules which have the $C=CH_2$ group show the expected band at 6 to 6.1$\mu$ which is due to the C=C stretching vibration. However, the three compounds which do not possess this group (2-octene, 3-octene, and 4-octene) show only very weak bands at this position. Since it is certain that such a frequency is present, and impossible that it be forbidden by any symmetry selection rules in molecules of so many possible configurations and of such low symmetry, it would seem that as regards the dipole change associated with double-bond vibration the molecules behave very nearly as *trans*-2-butene (double-bond vibration optically inactive) or *cis*-2-butene (double-bond band weak[1]). This lowering of intensity of C=C stretching frequencies indicates that caution must be used in taking the absence of a strong band at 6 to 6.1$\mu$ to be a criterion for the absence of double bonds. In contrast, the Raman frequency at *ca.* 1650 $cm^{-1}$ corresponding to the C=C vibration suffers no marked diminution in intensity when both carbons are substituted.

The vapor spectra show no essential differences from the liquid aside from the absence of a great many of the weaker bands due to the smaller amount of absorbing material.

[6] According to the method of preparation, the 3- and 4-octenes should be of the *trans*-configuration about the double bond, whereas the 2-octene may be a mixture of *cis*- and *trans*-. Cleveland (reference 4) discusses the preparation, and from his Raman work failed to find indications of the *cis*-form. From work on compounds studied subsequent to the writing of this paper, it appears that the strong 10.3$\mu$ infra-red band is characteristic of the *trans*-form of the CHR=CHR system. The *cis*-form shows a band of much lower intensity and more variable position in the 10 to 11$\mu$ region, and also a very strong band in the 14 to 16$\mu$ region. On this basis, the 14.2$\mu$ band observed in 2-octene would denote a few percent of *cis*-form, while the very strong 10.3$\mu$ band indicates the *trans*-form as the principal constituent. The absence of any analogous long wave band (14 to 15$\mu$) in the spectra of 3-octene and 4-octene then agrees with the method of preparation in indicating no *cis*-form.

# On the Quantum Correction for Thermodynamic Equilibrium

JOSEPH E. MAYER AND WILLIAM BAND
*Institute for Nuclear Studies, University of Chicago, Chicago, Illinois*

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The behavior of any system at high enough temperatures approaches that of its classical counterpart. The probability of any configurational position is then proportional to $\exp -U/kT$, with $U$ the potential energy. Wigner has shown that quantum-mechanical deviations, as the temperature is lowered, may be approximated by multiplication of this with $1-f$, where $f$ is a function proportional to $h^2$ and having terms in $T^{-2}$ and terms in $T^{-3}$. This type of approximation is unsatisfactory for a system of many degrees of freedom, that is, one of many dependent molecules. For such a system it is shown that instead of Wigner's approximation we may replace the classical potential $U$ in the exponent by $U-kTf$, where $f$ is the same as Wigner's function.

## INTRODUCTION

IN 1932 a paper with the same title as this was published by E. Wigner.[1] One of the results of the paper was the proof of an approximate expression which could be used to replace the exponent of the negative potential energy divided by $kT$ for the relative probability of a configuration in coordinate space. The expression obtained is satisfactory for a system of a limited number of degrees of freedom but cannot be used, without amplification, for a system consisting of many molecules for which the Hamiltonian is not separable in the coordinates of the different molecules. The difficulty in using Wigner's approximation for a system of many degrees of freedom lies in the fact that in this case *either* the quantum correction derived is entirely negligible, *or* the conditions under which it is a valid approximation are not fulfilled.

The probability, for a classical system, that the coordinates of $N$ molecules will have the value $\{N\}$ within the volume element $d\{N\}$ is proportional to $\exp(-U\{N\}/kT)$ where $U\{N\}$ is the potential energy as a function of the configurational coordinates $\{N\}$. Wigner shows that for a quantum-mechanical system the above expression may be multiplied by a factor $(1-f_N\{N\})$ where,

$$f_N=\frac{h^2}{48\pi^2k^2T^2}\sum_k\frac{1}{m_k}\frac{\partial^2U}{\partial x_k^2}-\frac{h^2}{96\pi^2k^3T^3}\sum_k\frac{1}{m_k}\left(\frac{\partial U}{\partial x_k}\right)^2, \quad (1)$$

in which the sums run over all Cartesian coordinates $k$, and $m_k$ is the mass of the particle whose coordinate is $x_k$. The above approximation is valid providing $f_N\{N\}\ll 1$ for all values of $\{N\}$, in which case the higher order terms which have been omitted are presumably actually negligible.

For a system of many interacting molecules, that is one for which there are very many degrees of freedom in which the Hamiltonian is not separable, one may *not* regard the probability as a product of terms like those above, one for each molecule. In this case either $f_N\{N\}\gg 1$ or the thermodynamic properties of the system differ negligibly from that of a classical one.

The demonstration of this statement is simple. There is an additive contribution $A_\tau$ to the Helmholtz free energy of the classical system equal to $-kT\ln Q_{\tau\,\mathrm{cl}}$ where

$$Q_{\tau\,\mathrm{cl}}=\int_V[\exp(-U\{N\}/kT)]d\{N\}. \quad (2)$$

For the quantum-mechanical system the contribution is $-kT\ln[Q_{\tau\,\mathrm{cl}}(1-\alpha)]$ where,

$$\alpha=\frac{1}{Q_{\tau\,\mathrm{cl}}}\int f_N\{N\}[\exp(-U\{N\}/kT)]d\{N\}, \quad (3)$$

so that the difference in Helmhotz free energy of the classical and quantum-mechanical system is $kT\ln(1-\alpha)=RT[N^{-1}\ln(1-\alpha)]$, with $N$ Avogadro's number. Now free energies of macroscopic systems are of the order $RT$, so that unless $N^{-1}\ln(1-\alpha)$ is not completely negligible compared to unity the properties of the system are those of the classical counterpart. However,

[1] E. Wigner, Phys. Rev. **40**, 749 (1932).

from (3) and (2) it is seen that if $f_N\{N\} \ll 1$, everywhere then $\alpha \ll 1$ and $N^{-1}\ln(1-\alpha) \cong -N^{-1}\alpha$, and the quantum-mechanical correction is some $10^{-23}$ times a small value.

In various important problems it is necessary to discuss assemblies of particles, and to consider the behavior of the assembly in the limit as the number of particles approaches infinity. In order to understand the transition in behavior of such an assembly as the temperature is lowered, and quantum restrictions begin to become noticeable, it seems advisable to extend Wigner's approximation.

### THE PROBABILITY INTEGRAL

The partition function $Q$ of a quantum-mechanical system may be defined as:

$$Q = \sum_\nu \exp(-E_\nu/kT), \tag{4}$$

in which the sum runs over all quantum numbers $\nu$ of the system, and $E_\nu$ is the energy of the system in the quantum state $\nu$. The Helmholtz free energy, $A$, of the system is

$$A = -kT \ln Q. \tag{5}$$

The probability that the system is in the quantum state $\nu$ is $Q^{-1}\exp(-E\nu/kT)$, and if it is in this state, $\psi_\nu^*\{N\}\psi_\nu\{N\}$ gives the probability density that the molecules are at the configurational position $\{N\}$, where $\psi_\nu$ is the normalized wave function associated with the quantum state $\nu$. The probability density of the position $\{N\}$ is then the sum:

$$P\{N\} = Q^{-1}\sum_\nu \psi_\nu^*\{N\}[\exp(-E_\nu/kT)]\psi_\nu\{N\}. \tag{6}$$

The function,

$$F_N\{N\} \equiv \sum_\nu \psi_\nu^*\{N\}[\exp(-E_\nu/kT)]\psi_\nu\{N\}, \tag{7}$$

is proportional to the probability density at the position $\{N\}$ and has the property that,

$$\int_V F_N\{N\}d\{N\} = Q, \tag{8}$$

where the integration runs over all configurational positions $\{N\}$ of the molecules in the volume $V$ of the system.

The semi-classical analog of $F_N$ is the integral,

$$F_{N\,\mathrm{cl}} = [1/\Pi_k(h^{3N_k}N_k!)] \times \int [\exp(-H/kT)]dp_{1x}\cdots dp_{Nz}, \tag{9}$$

where $H$ is the classical Hamiltonian expressed in the Cartesian coordinates of the individual point particles of the system and the integration extends over all momenta from $-\infty$ to $+\infty$. The factor in front of the integral normalizes $F_{N\,\mathrm{cl}}$ to make it consistent with the quantum-mechanical third law entropy, and does this by counting the number of quantum states in the classical phase volume $dW$ as $dW/\Pi_k h^{3N_k}N_k!$, where $N_k$ is the number of identical particles of type $k$ in the system. Since the Hamiltonian is in Cartesian coordinates, it includes an additive term $(1/2m_k)p_{ki}^2$ for each momentum $p_{ki}$ of particles of type $k$. The integration over the momenta,

$$\int [\exp-(1/2mkT)p^2]dp = (2\pi mkT)^{\frac{1}{2}},$$

then gives

$$F_{N\,\mathrm{cl}}\{N\} = \left[\prod_k \frac{(2\pi mkT/h^2)^{3N_k/2}}{N_k!}\right] \times \exp - U_N\{N\}/kT, \tag{10}$$

for the classical function, $F_{N\,\mathrm{cl}}$.

We return, now, to the quantum-mechanical expression (7). If $\mathbf{H}$ is the quantum-mechanical Hamiltonian operator of the system, $\mathbf{H}\psi_\nu = E_\nu\psi_\nu$, and $\mathbf{H}^n\psi_\nu = E_\nu{}^n\psi_\nu$, where by $\mathbf{H}^n$ we mean that the operation $\mathbf{H}$ is repeated $n$ times. It follows that if we define,

$$\exp(-\mathbf{H}/kT) = \sum_{n\geq 0}[(-1/kT)^n/n!]\mathbf{H}^n, \tag{11}$$

we may replace $\exp(-E_\nu/kT)$ in (7) by $\exp(-\mathbf{H}/kT)$ and write:

$$F_N = \sum_\nu \psi_\nu^*[\exp(-\mathbf{H}/kT)]\psi_\nu. \tag{12}$$

The sum of (12) is invariant under a transformation to new wave functions $\varphi_\kappa$. That is, if $\varphi_\kappa$ is a member of a complete set of orthogonal normalized functions of the coordinates $\{N\}$, obeying the same boundary and symmetry contions as the eigenfunctions $\psi_\nu$, we may write:

$$F_N = \sum_\kappa \varphi_\kappa^*[\exp(-\mathbf{H}/kT)]\varphi_\kappa. \tag{13}$$

This is readily proved if we insert the development $\psi_\nu = \sum_\kappa a_{\nu\kappa}\varphi_\kappa$ in (12) and make use of the fact that if the $\psi_\nu$ and $\varphi_\kappa$ are normalized and

orthogonal to other members of their respective sets, $\sum_\nu a_{\nu\kappa}^* a_{\nu\kappa'} = 1$ if $\kappa \equiv \kappa'$ and zero otherwise.

We now use simple products of plane wave functions for $\varphi_\kappa$, namely:

$$\varphi_\kappa = \prod_{j=1}^{j=N} (1/\sqrt{V}) \exp(2\pi i/h)\mathbf{p}_j\mathbf{r}_j, \tag{14}$$

where $\mathbf{r}_j$ is the position vector,

$$\mathbf{r}_j = x_j, y_j, z_j, \tag{15}$$

of the particle $j$, and $\mathbf{p}_j$ is a three-component vector,

$$\mathbf{p}_j = p_{jx}, p_{jy}, p_{jz}, \tag{16}$$

having the significance of the momentum of the particle $j$ in the state $\varphi_\kappa$. The momentum components, $p_{jx}$, are quantized to take the values,

$$p_{jx} = h/\lambda_x = \kappa_{jx} h V^{-\frac{1}{3}}, \tag{17}$$

in the cubic box of volume $V$, with $\kappa_{jx}$ an integer. The set of these integers,

$$\kappa \equiv \kappa_{1x}, \kappa_{1y}, \kappa_{1z}, \cdots, \kappa_{jx}, \cdots \kappa_{Nz}, \tag{18}$$

comprise the quantum number $\kappa$ of the state. It is convenient to use the symbol,

$$\mathbf{p}_\kappa = \mathbf{p}_1, \mathbf{p}_2, \cdots, \mathbf{p}_N, \tag{19}$$

for the $3N$-dimensional momentum vector, and,

$$\mathbf{r} = \mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N,$$

for the $3N$-dimensional configuration vector so that we may write,

$$\varphi_\kappa = (1/V^{N/2}) \exp(2\pi i/h)(\mathbf{p}_\kappa \cdot \mathbf{r}). \tag{20}$$

The Hamiltonian operator $\mathbf{H}$, written in Cartesian coordinates is,

$$\mathbf{H} = \frac{1}{2m}\frac{h}{2\pi i}\nabla \cdot \frac{h}{2\pi i}\nabla + U, \tag{21}$$

if all the masses are equal to $m$, where,

$$\nabla = \sum_j \mathbf{x}_j \frac{\partial}{\partial x_j} + \mathbf{y}_j \frac{\partial}{\partial y_j} + \mathbf{z}_j \frac{\partial}{\partial z_j}, \tag{22}$$

with $\mathbf{x}_j$ unit vector along the $x$ axis of molecule $j$. We prefer to retain the simple expression (21) even for the case that all masses are not equal since it reveals the dimensionality of the ensuing equations. It may be made applicable to cases of different kinds of molecules by defining,

$$\nabla = \sum_j \left(\frac{m}{m_j}\right)^{\frac{1}{2}} \left(\mathbf{x}_j \frac{\partial}{\partial x_j} + \mathbf{y}_j \frac{\partial}{\partial y_j} + \mathbf{z}_j \frac{\partial}{\partial z_j}\right), \tag{22'}$$

for the general case.

If all masses are equal, and $\nabla$ is defined by (22), then,

$$(h/2\pi i)\nabla \varphi_\kappa = \varphi_\kappa \mathbf{p}_\kappa. \tag{23}$$

If we redefine $\mathbf{p}_\kappa$ to be the $3N$-dimensional vector with components $(m/m_j)^{\frac{1}{2}} p_{jx}$ in (23) then this equation is valid even if $\nabla$ is given by (22'). The operation of $\mathbf{H}$ on any product, $\varphi_\kappa F$, of $\varphi_\kappa$ and a function, $F$, of the coordinates, yields,

$$\mathbf{H}\varphi_\kappa F = \varphi_\kappa \left[\frac{1}{2m}\mathbf{p}_\kappa \cdot \mathbf{p}_\kappa + U + \frac{1}{2m}\left(\frac{h}{2\pi i}\nabla + 2\mathbf{p}_\kappa\right) \cdot \frac{h}{2\pi i}\nabla\right] F. \tag{24}$$

Let us use the symbols:

$$H_\kappa = \frac{1}{2m}\mathbf{p}_\kappa \cdot \mathbf{p}_\kappa + U, \tag{25}$$

for the classical Hamiltonian of the system at the position $\{N\}$ when the momenta components are those of the state $\kappa$, and,

$$\mathbf{O}_\kappa = \frac{1}{2m}\left(\frac{h}{2\pi i}\nabla + 2\mathbf{p}_\kappa\right) \cdot \frac{h}{2\pi i}\nabla, \tag{26}$$

for the operator; one may then shorten (24) to,

$$\mathbf{H}\varphi_\kappa F = \varphi_\kappa (H_\kappa + \mathbf{O}_\kappa) F. \tag{27}$$

The operation $\mathbf{H}\varphi_\kappa$ is $\varphi_\kappa(H_\kappa + \mathbf{O}_\kappa)$ if we understand $(H_\kappa + \mathbf{O}_\kappa)$ to mean the operation on the constant function unity; then actually $H_\kappa + \mathbf{O}_\kappa = H_\kappa$ since $\mathbf{O}_\kappa$ operating on unity is zero. We may thus formally write:

$$\mathbf{H}^n \varphi_\kappa = \varphi_\kappa (H_\kappa + \mathbf{O}_\kappa)^n,$$

for, operating on this with $\mathbf{H}$, writing $(H_\kappa + \mathbf{O}_\kappa)^n$ for $F$ in (27), one obtains from the equation for $\mathbf{H}^n$ the analogous equation for $\mathbf{H}^{n+1}$, namely

$$\mathbf{H}^{n+1}\varphi_\kappa = \varphi_\kappa (H_\kappa + \mathbf{O}_\kappa)(H_\kappa + \mathbf{O}_\kappa)^n = \varphi_\kappa (H_\kappa + \mathbf{O}_\kappa)^{n+1}.$$

Since the equation for $n = 1$ is identical with $F = 1$ in (27), it is true by induction for any $n$.

We thus obtain:

$$\sum_{n\geq 0}[(-1/kT)^n/n!]\mathbf{H}^n\varphi_\kappa = \varphi_\kappa\sum_{n\geq 0}[(-1/kT)^n\cdot n!][H_\kappa+\mathbf{O}_\kappa]^n,$$

and,

$$[\exp(-\mathbf{H}/kT)]\varphi_\kappa=\varphi_\kappa\exp-(H_\kappa+\mathbf{O}_\kappa)/kT. \quad (28)$$

Since $\varphi_\kappa^*\varphi_\kappa\equiv 1/V^N$ for all values of $\{N\}$, we find from (13) that,

$$F_N\{N\}=V^{-N}\sum_\kappa\exp-(H_\kappa+\mathbf{O}_\kappa)/kT, \quad (29)$$

where we understand that the operation indicated is to be carried out on the constant function unity.

If the volume $V$ is large, the quantized values of $\mathbf{p}_\kappa$ lie extremely close together, and we may replace summation over the quantum numbers $\kappa$ by integration, and if we so choose, may carry out this integration in the $\mathbf{p}$ space. It is seen from (17) that the volume element $dp_{1x}$, $dp_{1y}$, $\cdots$, $dp_{Nz}$ includes $V^N/h^{3N}dp_{1x}\cdots dp_{Nz}$ values of $\kappa$. We may therefore multiply (28) by $V^N/h^{3N}$ and integrate over $dp$.

However, we are then tacitly assuming that every value of $\kappa=\kappa_{1x},\cdots\kappa_{Nz}$, leads to an allowed quantum state of the system. But for real systems we must use only eigenfunctions which are either symmetric or antisymmetric in all permutations of identical particles. The detailed study of this case will be made in a subsequent paper. For the present we shall be content with the approximation that there are about $(\Omega/\Pi_k N_k!)$ symmetric or antisymmetric states in a random range of $\kappa$ including $\Omega$ states. We must therefore multiply (28) by $V^n/\Pi_k(h^{3N_k}N_k!)$ in order to replace the summation by integration.

Finally, omitting the subscripts $\kappa$ on $H$ and $\mathbf{O}$, so that these are regarded as functions of the continuously varying vector $\mathbf{p}$, of $3N$ dimensions, we have

$$F_N\{N\}=\left(\prod_k\frac{1}{h^{3N_k}N_k!}\right)\times\int[\exp-(H+\mathbf{O})/kT]dp_{1x}\cdots dp_{Nz}, \quad (30)$$

for a quantum-mechanical system. This expression is seen to differ from (9) for the classical system only in the replacement of $H$ by $H+\mathbf{O}$.

## EVALUATION OF $[\exp-(H+\mathbf{O})/kT]$

In order to make use of the simple but symbolic expression (30) it is necessary to evaluate $\exp-(H+\mathbf{O})/kT$ as a quantity, rather than as an operation on unity.

It is convenient, at this stage, to simplify the expression somewhat. We introduce a dimensionless momentum vector:

$$\mathbf{p}^*=(2mkT)^{-\frac{1}{2}}\mathbf{p}, \quad (31)$$

and

$$\lambda=[h^2/(8\pi^2mkT)]^{\frac{1}{2}}, \quad (32)$$

of the dimensions of length. The operator, $\mathbf{O}$, divided by $kT$ is then,

$$\mathbf{O}^*=\mathbf{O}/kT=-\lambda^2\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}-2i\lambda\mathbf{p}^*\cdot\boldsymbol{\nabla}. \quad (33)$$

By using,

$$U^*=U/kT, \quad (34)$$

the Hamiltonian, $H$, divided by $kT$ becomes,

$$H^*=H/kT=\mathbf{p}^*\cdot\mathbf{p}^*+U^*. \quad (35)$$

We seek the functional representation of $\exp-(H^*+\mathbf{O}^*)$, which is a sum of powers, $(-H^*-\mathbf{O}^*)^n/n!$, operating on unity. Each such power is a sum of products of functions, the general factor being itself a scalar product of tensor factors. It is simplest to write the correct expression for $(H^*+\mathbf{O}^*)^n$, and to prove its correctness.

We define functions $\Theta_{\nu,\mu}$, for $\nu\geq 1$, $\mu\geq\nu-1$, by the equation,

$$\Theta_{1,0}=H^*=\mathbf{p}^*\cdot\mathbf{p}^*+U^*, \quad (36)$$

and the recursion relation:

$$\Theta_{\nu,\mu}=\frac{1}{\nu+\mu}\left\{(\mathbf{O}^*\Theta_{\nu,\mu-1}) - \sum_{\nu'=1}^{\nu'=\nu-1}\sum_{\mu'=\nu'-1}^{\mu'=\mu-\nu+\nu'}\lambda^2\boldsymbol{\nabla}\Theta_{\nu-\nu',\mu-\mu'-1}\cdot\boldsymbol{\nabla}\Theta_{\nu',\mu'}\right\}. \quad (37)$$

We shall finally prove that,

$$[\exp-(H^*+\mathbf{O}^*)]=\exp\sum_{\nu\geq 1}\sum_{\mu\geq\nu-1}(-)^{\nu+\mu}\Theta_{\nu,\mu}. \quad (38)$$

We note first that, given Eq. (36) for $\Theta_{1,0}$, Eq. (37) is a sufficient condition for the determination of the functions $\Theta_{\nu,\mu}$, since we can proceed by steps of unity in $\mu$ and $\nu$ from the first mem-

ber, $\nu=1$, $\mu=0$, to any higher member of the series. The expression on the right involves only the lower, and already determined members, at each step.

Indeed, we may write the first few members of the series, directly, as:

$$\Theta_{1,1}=\tfrac{1}{2}\mathbf{O}^*\Theta_{1,0}=-\tfrac{1}{2}\lambda^2\nabla\cdot\nabla U^*-i\lambda\mathbf{p}^*\cdot\nabla U^*, \quad (39)$$

$$\Theta_{1,2}=(1/3)\mathbf{O}^*\Theta_{1,1}=(1/6)\lambda^4(\nabla\cdot\nabla)^2U^* +(2/3)i\lambda^3(\nabla\cdot\nabla)(\mathbf{p}^*\cdot\nabla)U^* -(2/3)\lambda^2(\mathbf{p}^*\cdot\nabla)^2U^*, \quad (40)$$

$$\Theta_{2,1}=-(1/3)\lambda^2\nabla\Theta_{1,0}\cdot\nabla\Theta_{1,0} =-(1/3)\lambda^2\nabla U^*\cdot\nabla U^*, \quad (41)$$

which, incidentally, include all members of the series which have terms of order quadratic or lower in $\lambda$.

We now wish to prove that if we define:

$$T_{\rho(n)}=\prod_{\nu,\mu}[\Theta_{\nu,\mu}{}^{\rho(\nu,\mu)}/\rho(\nu,\mu)!] \quad (42)$$

in which $\rho(n)$ is a set,

$$\rho(n)=\rho(1,0),\rho(1,1),\rho(1,2),\cdots,\rho(2,1),\cdots, \quad (43)$$

obeying the relation,

$$\sum_{\nu\geq 1}\sum_{\mu\geq\nu-1}(\nu+\mu)\rho(\nu,\mu)=n, \quad (44)$$

then,

$$(H^*+\mathbf{O}^*)^n=n!\sum_{\rho(n)}T_{\rho(n)}, \quad (45)$$

in which the summation runs over all values of the set $\rho(n)$, Eq. (43), which obey the relation (44).

In the first place we call attention to the fact that the significance of the indicial $\nu$ and $\mu$ on the functions $\Theta_{\nu,\mu}$ of Eqs. (36) and (37) is that $\nu$ is the power of $H^*$ occurring in $\Theta_{\nu,\mu}$, and $\mu$ is the order of the operation $\mathbf{O}^*$, or $\nabla\Theta\cdot\nabla\Theta$, occurring in $\Theta_{\nu,\mu}$. The power, or order, of the operator is always half the sum of the powers of $\mathbf{p}^*$ and $\lambda$, Eqs. (36), (39)–(41). The condition (44) on the powers, $\rho(\nu,\mu)$, of the various functions $\Theta_{\nu,\mu}$ in the product $T_{\rho(n)}$, Eq. (42), is just the condition that the sum of the powers of $H^*$ and $\mathbf{O}^*$ shall be $n$.

In order to prove Eq. (45) we use the method of induction. The first step is trivial, and consists of noting that $H^*+\mathbf{O}^*$ to the first power, operating on unity is just $H^*=\Theta_{1,0}$, and that the right-hand side of (45) with $n=1$ is just $\Theta_{1,0}$. Thus (45) is correct for $n=1$. The second step is less trivial, and consists of showing that if (45) holds for an $n$ it therefore holds for $n+1$.

To prove the latter statement we operate on (45) with $H^*+\mathbf{O}^*$, obtaining:

$$(H^*+\mathbf{O}^*)(H^*+\mathbf{O}^*)^n=(H^*+\mathbf{O}^*)^{n+1}=(H^*+O^*)n!\sum_{\rho(n)}T_{\rho(n)}$$

$$=n!\sum_{\rho(n)}T_{\rho(n)}\Big\{\Theta_{1,0}+\sum_{\nu\geq 1}\sum_{\mu\geq\nu-1}\rho(\nu,\mu)(\mathbf{O}^*\Theta_{\nu,\mu})/\Theta_{\nu,\mu}$$

$$-\lambda^2\sum_{\nu\geq 1}\sum_{\mu=\nu-1}\sum_{\nu'\geq 1}\sum_{\mu'\geq\nu'-1}\rho(\nu,\mu)[\rho(\nu',\mu')-\delta(\nu,\nu')\delta(\mu,\mu')]\frac{\nabla\Theta_{\nu,\mu}\cdot\nabla\Theta_{\nu'\mu'}}{\Theta_{\nu,\mu}\Theta_{\nu',\mu'}}\Big\}. \quad (46)$$

Because of the significance of $\nu$ and $\mu$ mentioned in the last paragraph but one, we may now write:

$$\Theta_{1,0}\sum_{\rho(n)}T_{\rho(n)}=\sum_{\rho(n+1)}\rho(1,0)T_{\rho(n+1)}, \quad (47)$$

$$\sum_{\rho(n)}\frac{\rho(\nu,\mu)}{\Theta_{\nu,\mu}}T_{\rho(n)}=\frac{1}{\Theta_{\nu,\mu+1}}\sum_{\rho(n+1)}\rho(\nu,\mu+1)T_{\rho(n+1)}, \quad (48)$$

and

$$\sum_{\rho(n)}\frac{\rho(\nu,\mu)[\rho(\nu',\mu')-\delta(\nu,\nu')\delta(\mu,\mu')]}{\Theta_{\nu,\mu}\Theta_{\nu',\mu'}}T_{\rho(n)}=\frac{1}{\Theta_{\nu+\nu',\mu+\mu'+1}}\sum_{\rho(n+1)}\rho(\nu+\nu',\mu+\mu'+1)T_{\rho(n+1)}. \quad (49)$$

With these three equations in (46) we find that:

$$(H^*+\mathbf{O}^*)^{n+1}=(n+1)!\sum_{\rho(n+1)}T_{\rho(n+1)}\frac{1}{n+1}\Big\{\rho(1,0)$$

$$+\sum_{\nu\geq 1}\sum_{\mu\geq 1 \text{ or } \kappa-1}\frac{\rho(\nu,\mu)}{\Theta_{\nu,\mu}}\Big[\mathbf{O}^*\Theta_{\nu,\mu-1}-\lambda^2\sum_{\nu'=1}^{\nu'=\nu-1}\sum_{\mu'=\nu'-1}^{\mu=\mu-\nu+\nu'}\boldsymbol{\nabla}\Theta_{\nu-\nu',\mu-\mu'-1}\cdot\boldsymbol{\nabla}\Theta_{\nu',\mu'}\Big]\Big\}, \quad (50)$$

which, in view of (37) is

$$(H^*+O^*)^{n+1}=(n+1)!\sum_{\rho(n+1)}T_{\rho(n+1)}\frac{1}{n+1}\sum_{\nu\geq 1}\sum_{\mu\geq \nu-1}(\nu+\mu)\rho(\nu,\mu). \quad (51)$$

The final sum is just $n+1$, when Eq. (44) is used and one remembers that the sets $\rho$ belong to the subset $\rho(n+1)$. We thus have,

$$(H^*+O^*)^{n+1}=(n+1)!\sum_{\rho(n+1)}T_{\rho(n+1)}, \quad (52)$$

and have proved Eq. (45) to be correct.

Using (45) we find:

$$\exp-(H^*+\mathbf{O}^*)=\sum_{n\geq 0}(-)^n(H^*+\mathbf{O}^*)^n/n!=\sum_{n\geq 0}(-)^n\sum_{\rho(n)}T_{\rho(n)}$$

$$=\sum_{\rho(\nu,\mu)\geq 0}\prod_{\nu,\mu}[((-)^{\nu+\mu}\Theta_{\nu,\mu})^{\rho(\nu,\mu)}/\rho(\nu,\mu)!]=\exp\sum_{\nu\geq 1}\sum_{\mu\geq \nu-1}(-)^{\nu+\mu}\Theta_{\nu,\mu}, \quad (53)$$

where the summation over $n$ *and* $\rho(n)$ means summation over all sets $\rho$.

We have thus proved Eq. (38). Using Eq. (30) one sees that if one writes,

$$H_Q=-kT\sum_{\nu\geq 1}\sum_{\mu\geq \nu-1}(-)^{\nu+\mu}\Theta_{\nu,\mu}, \quad (54)$$

then

$$F_N\{N\}=\prod_k[h^{3N_k}N_k!]^{-1}\int\int\cdots\int[\exp-H_Q/kT]dp_{1x}\cdots dp_{zN}, \quad (55)$$

and $H_Q$ replaces the classical Hamiltonian, $H$, in the exponent. With Eqs. (36), (39)–(41) for the first members of the series we see that,

$$H_Q/kT=\mathbf{p}^*\cdot\mathbf{p}^*+U^*+i\lambda\mathbf{p}^*\cdot\boldsymbol{\nabla}U^*+\lambda^2[\tfrac{1}{2}\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}U^*-(1/3)\boldsymbol{\nabla}U^*\cdot\boldsymbol{\nabla}U^*-(2/3)(p^*\cdot\boldsymbol{\nabla})^2U^*]+\cdots, \quad (56)$$

up to quadratic powers in $\lambda$.

## INTEGRATION OVER THE MOMENTA

We now wish to carry out the integration over the momenta of $\exp-H_Q/kT$. Let us collect those additive terms of $H_Q/kT$ Eq. (56), which contain one component, $p_i^*$, of the normalized momentum vector, $\mathbf{p}^*$. These are:

$$p_i^{*2}+i\lambda p_i^*\partial U^*/\partial x_i-(2/3)\lambda^2p_i^{*2}\partial^2U^*/\partial x_i^2-(4/3)\lambda^2p_i^*\sum_{j\neq i}p_j^*\partial^2U^*/\partial x_i\partial x_j.$$

This can be written as a perfect square, plus terms not containing $p_i^*$, namely as:

$$[1-(2/3)\lambda^2\partial^2U^*/\partial x_i^2]\left\{p_i^*+\frac{\frac{1}{2}i\lambda\partial U^*/\partial x_i-(2/3)\lambda^2\sum_{j\neq 1}p_j^*\partial^2U^*/\partial x_i\partial x_j}{1-(2/3)\lambda^2\partial^2U^*/\partial x_j^2}\right\}^2$$

$$-\left\{\frac{\frac{1}{2}i\lambda\partial U^*/\partial x_i-(2/3)\lambda^2\sum_{j\neq i}p_j^*\partial^2U^*/\partial x_i\partial x_j}{1-(2/3)\lambda^2\partial^2U^*/\partial x_i^2}\right\}^2. \quad (57)$$

The integration of the exponent of the negative of the expression (57) over $dp_i=(2m_ikT)^{\frac{1}{2}}dp_i^*$, and division of the result by $h$, leads to the factor:

$$\left(\frac{2\pi m_ikT}{h^2}\right)^{\frac{1}{2}}[1-(2/3)\lambda^2\partial^2U^*/\partial x_i^2]^{-\frac{1}{2}}\exp\left\{\frac{\frac{1}{2}i\lambda\partial U^*/\partial x_i-(2/3)\lambda^2\sum_{j\neq i}p_j^*\partial^2U^*/\partial x_i\partial x_j}{1-(2/3)\lambda^2\partial^2U^*/\partial x_i^2}\right\}^2,$$

which then multiplies the integrand remaining for integration over the other momenta components. If we use $[1-\alpha]^{-\frac{1}{2}}=\exp[-\frac{1}{2}\ln(1-\alpha)]\cong\exp(+\frac{1}{2}\alpha)$, and retain in the exponent only terms quadratic in $\lambda$, one finds:

$$\left(\frac{2\pi m_ikT}{h^2}\right)^{\frac{1}{2}}\exp\{-(1/4)\lambda^2(\partial U^*/\partial x_i)^2+(1/3)\lambda^2\partial^2U^*/\partial x_i^2\},$$

as the approximate expression for this factor introduced by integration over the single component $i$ of momentum.

The result of integration of (55) over all momentum components is then:

$$F_N\{N\}=\left\{\prod_k\left(\frac{2\pi m_kkT}{h^2}\right)^{3N_k/2}\frac{1}{N_k!}\right\}\exp-U_Q/kT, \quad (58)$$

where

$$U_Q/kT=U^*+\lambda^2[(1/6)\nabla\cdot\nabla U^*-(1/12)\nabla U^*\cdot\nabla U^*]+\cdots, \quad (59)$$

or

$$U_Q=U+\sum_i\left[(1/6)\lambda_i^2\frac{\partial^2U}{\partial x_i^2}-\frac{1}{12kT}\lambda_i^2\left(\frac{\partial U}{\partial x_i}\right)^2\right]+\cdots, \quad (59')$$

up to terms quadratic in,

$$\lambda_i=[h^2/8\pi^2m_ikT]^{\frac{1}{2}}. \quad (60)$$

If we use,

$$\exp(-U_Q/kT)=[\exp(-U/kT)][\exp(U-U_Q/kT],$$

and expand,

$$\exp(U-U_Q)/kT\cong 1-\frac{U_Q-U}{kT}=1-\sum_i(1/6)\lambda_i^2\frac{\partial^2U}{\partial x_i^2}+(1/12)(1/kT)\lambda_i^2\left(\frac{\partial U}{\partial x_i}\right)^2, \quad (61)$$

we obtain Wigner's expression, Eq. (1).

### A SYSTEM WITH PAIR POTENTIALS

It is possible to show, by a somewhat involved method, that the general system for which $F_N$ is given by (58) with $U_Q$ defined in Eq. (59) does deviate from classical behavior with terms proportional to $h^2/T^2$. It is, however, probably more interesting to examine a special case, namely that in which the classical potential energy, $U$, can be written as a sum of terms, each involving only pairs of molecules:

$$U=\sum_{N\geq i>j\geq 1}\sum u_{ij}(r_{ij}). \tag{62}$$

In Eq. (62) we have tacitly assumed that the mutual potential energy, $u_{ij}$, between the pair, $i$, $j$, of molecules, depends only on the magnitude of the distance, $r_{ij}$, between their centers of mass.

We have:

$$\frac{\partial u_{ij}}{\partial x_i}=\frac{\partial u_{ij}}{\partial r_{ij}}\frac{\partial r_{ij}}{\partial x_i}=\frac{x_{ij}}{r_{ij}}u'_{ij}, \tag{63}$$

where,

$$u'_{ij}=du_{ij}/dr_{ij}, \tag{64}$$

$$x_{ij}=x_i-x_j, \tag{65}$$

and,

$$\frac{\partial^2 u_{ij}}{\partial x_i^2}=u''_{ij}\left(\frac{x_{ij}}{r_{ij}}\right)^2+\frac{u'_{ij}}{r_{ij}}\left[1-\left(\frac{x_{ij}}{r_{ij}}\right)^2\right], \tag{66}$$

where,

$$u''_{ij}=d^2u_{ij}/dr_{ij}^2. \tag{67}$$

Summing over all molecules, and all three axes for each, we find:

$$\sum_{i=1}^{i=3N}\partial^2U/\partial x_i^2=2\sum_{N\geq i>j\geq 1}\sum[u''_{ij}+2u'_{ij}/r_{ij}]. \tag{68}$$

For $\sum\lambda_i^2(\partial U/\partial x_i)^2$ we obtain:

$$\sum_{i=1}^{i=3N}\lambda_i^2(\partial U/\partial x_i)^2=2\sum_{N\geq i>j\geq 1}\sum\lambda_i^2(u'_{ij})^2+\sum_{N\geq i>}\sum_{j>k\geq 1}\sum f_{ijk}, \tag{69}$$

where,

$$f_{ijk}=\lambda_i^2\frac{u'_{ij}u'_{ik}}{r_{ij}r_{ik}}(r_{ik}^2+r_{ij}^2-r_{jk}^2)+\lambda_j^2\frac{u'_{ij}u'_{jk}}{r_{ij}r_{jk}}(r_{ij}^2+r_{jk}^2-r_{ik}^2)+\lambda_k^2\frac{u'_{ik}u'_{jk}}{r_{ik}r_{jk}}(r_{ik}^2+r_{jk}^2-r_{ij}^2). \tag{70}$$

Using Eqs. (62), (68), and (69) in (59′) one finds:

$$U_Q=\sum_{N\geq i>j\geq 1}\sum\Big[u_{ij}+(1/6)(\lambda_i^2+\lambda_j^2)u''_{ij}+(1/3)(\lambda_i^2+\lambda_j^2)u'_{ij}/r_{ij}$$

$$-\frac{1}{12kT}(\lambda_i^2+\lambda_j^2)(u'_{ij})^2\Big]-\sum_{N\geq i>}\sum_{j>k\geq 1}\sum\frac{1}{12kT}f_{ijk}, \tag{71}$$

for this case.

Now the energy of the system is given by the equation,

$$E=kT^2\partial \ln Q/\partial T, \tag{72}$$

or since $\int F_N d\{N\}=Q$, with Eq. (58) for $F_N$ and (71) for $U_Q$, and remembering that $\lambda_i$, Eq. (60) is proportional to $T^{-\frac{1}{2}}$ one finds:

$$E=3NkT+Q^{-1}\int\int_V\cdots\int F_N\{N\}\Big\{\sum_{N\geq i>j\geq 1}\Big[u_{ij}+\tfrac{1}{3}(\lambda_i^2+\lambda_j^2)u''_{ij}+\tfrac{2}{3}(\lambda_i^2+\lambda_j^2)u'_{ij}/r_{ij}$$
$$-\frac{1}{4kT}(\lambda_i^2+\lambda_j^2)(u'_{ij})^2\Big]-\frac{1}{4kT}\sum_{N\geq i>j>k\geq 1}f_{ijk}\Big\}d\{N\}. \tag{73}$$

Let us, for the sake of simplicity, restrict ourselves to the case that all molecules are identical. In this case if,

$$\rho=N/V, \tag{74}$$

is the concentration in molecules per unit volume, then,

$$\rho^n F_n(\rho, T, \{n\})=\frac{N^n}{Q}\int\int_V\cdots\int F_N\{N\}d\{N-n\}, \tag{75}$$

is the probability density that $n$ molecules will be found at the configurational position $\{n\}$, irrespective of the positions of other molecules in the system. In Eq. (73) there will be $N(N-1)/2\cong N^2/2$ identical terms involving pairs of molecules, $i$, $j$, in the double summation, and $N(N-1)(N-2)/6\cong N^3/6$ triples, $i$, $j$, $k$, in the triple summation. If we integrate (73) over the coordinates of all molecules except some particular pair or triple in the respective terms, and use (75), we find:

$$E=3NkT+\tfrac{1}{2}\rho^2\int\int_V u_{ij}F_2(\rho, T, \{i, j\})d(i)d(j)+\tfrac{1}{2}\rho^2\lambda^2\int\int_V\Big[\frac{2}{3}u''_{ij}+\frac{4}{3}u'_{ij}\Big/r_{ij}-\frac{1}{2kT}(u'_{ij})^2\Big]$$
$$\times F_2(\rho, T, \{i, j\})d(i)d(j)-\frac{\rho^3}{24kT}\int\int\int_V f_{ijk}F_3(\rho, T, \{i, j, k\})d(i)d(j)d(k). \tag{76}$$

The first term, $3NkT$, in (76) is the classical kinetic energy. The second term, the integral of $u_{ij}$ is the average of the potential energies. The remaining terms involving integrations over pairs and triples of molecules are all proportional to $h^2$. The first two terms in the brackets of the pair integration are proportional to $T^{-2}$, and the last term in the pair integral, as well as the triple integral is proportional to $T^{-3}$. The triple integral, proportional to $\rho^3$ is relatively unimportant in an imperfect gas, but is presumably not of lesser importance in condensed systems.

It should be recognized, however, that $F_2$ and $F_3$ are different from the corresponding distribution functions for the classical system, and therefore the average potential energy is different in the system perturbed by quantum mechanical effects than it is in the classical system. It is tedious, but not difficult, to evaluate these differences in the distribution functions. As might be expected, they turn out, in first approximation, to be proportional to $h^2$.

# Letters to the Editor

*THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.*

## *Acta Crystallographica*

A SPECIAL international organization, formed largely for this purpose, is planning the publication of a journal to perform the services formerly rendered by the *Zeitschrift für Kristallographie*. *Acta Crystallographica*, as it will be called, will be published either in England or America and, while French, German, and Russian will be permitted languages, the bulk of the journal will be in English. It is expected that there will be six issues per year totaling approximately 1000 pages. The price to individual subscribers is tentatively set at $10.00 a year.

The American representatives in the international organization are extremely anxious to obtain a good idea of the probable circulation of the journal in North America. Any reader of this notice who would, or who might, subscribe to *Acta Crystallographica* is urged to send a note or postcard to that effect addressed to: Dr. Henry A. Barton, American Institute of Physics, 57 East 55 Street, New York 22, New York.

## Differences in Mass Spectra of $H_2$ and $D_2$

NORMAN BAUER AND J. Y. BEACH
*California Research Corporation, Richmond Laboratories, Richmond, California*
February 4, 1947

BLEAKNEY, Condon, and Smith[1] refer to unpublished work of J. A. Hipple which indicated a large difference in the yield of monatomic ions produced from $H_2$ and $D_2$ by impact with 22-volt electrons. These authors expect such a difference in behavior from a consideration of the Franck-Condon principle and the differences in zero point amplitude of vibration for $H_2$ and $D_2$. D. P. Stevenson[2] has recently made a quantitative estimate of the effect, based on these principles. If this theory proves adequate for $H_2$ and $D_2$, it may be of importance in estimating isotope effects in mass spectra of other molecules, for instance $C_2H_2D_2$,[3] and $CH_3D$.[4]

We wish to report a comparison of intensities (maximum ion currents) of $H^+$ and $D^+$, relative to $H_2^+$ and $D_2^+$, respectively, obtained with the Consolidated Engineering Corporation mass spectrometer (180° type) for a range of electron impact energies. The $H_2$ (100 percent) and $D_2$ (97.5 percent $D_2$, 2.5 percent HD) were found to contain no impurities which could appreciably contribute to $m/e=1$, 2, or 4. Monatomic and diatomic ion peaks were recorded in close succession by electric scanning, this being repeated over a range of nominal electron energies at intervals of 1 to 6 volts, at constant ionizing current. Nominal values of electron energy were corrected as previously described[4] and the equal appearance potentials of $H_2^+$ and $D_2^+$ agreed within 0.5 volt with Bleakney's[5] value for $H_2^+$. Above 35 volts, secondary electrons were eliminated from the ionizing region. Observed peak heights were corrected for the decrease caused by pressure change during a run. The ratios $r_H=(H^+/H_2^+)$ and $r_D=(D^+/D_2^+)$ were obtained at various energies by interpolation from the ionizing efficiency curves. The results are given in Table I.

Before conclusions can be drawn from the table we must take into account the discrimination characteristics of the particular mass spectrometer. The data of Washburn and Berry[6] indicate that, for the Consolidated instrument, the true relative abundances of ions from *n*-butane differ from the observed intensity ratios by no more than about 10 percent when the kinetic energy of the ions does not greatly exceed thermal energies and when relatively high ($\sim$1000 volts) values of the ion accelerating voltage ($V_{ia}$) are used. Our data for $H_2$ and $D_2$ around 30 volts should conform to this limit since it is known,[5,7] that the monatomic ions from $H_2$ produced below 30 volts have very small excess kinetic energy and since $V_{ia}$ was high (3200 volts for $H^+$, 1600 volts for $H_2^+$ and $D^+$, 800 volts for $D_2^+$) in our experiments. In support of this belief is the fact that we obtained an ion intensity per electron per unit pressure (sensitivity) for $D_2^+$ which differed from that for $H_2^+$ by only about 10 percent ($H_2^+ > D_2^+$) in a series of six pairs of careful comparisons.

At electron energies higher than 30 volts, an appreciable fraction of the $H^+$ ions are known to be formed with excess kinetic energy. However, this excess is so great (at least 5 to 11 volts) that the discrimination against these ions should be sufficient to prevent them from making an

TABLE I.

| Electron energy, volts | $r_H=(H^+/H_2^+)\times100$ | $r_D=(D^+/D_2^+)\times100$ | $R^*=r_H/r_D$ |
|---|---|---|---|
| 30 | 0.58 | 0.38 | 1.5 ±0.2 |
| 35 | 1.04 | 0.68 | 1.5 ±0.2 |
| 40 | 1.69 | 0.93 | 1.8 ±0.2 |
| 45 | 2.02 | 1.08 | 1.9 ±0.2 |
| 50 | 2.37 | 1.23 | 1.9 ±0.2 |
| 55 | 2.52 | 1.30 | 1.9 ±0.2 |
| 60 | 2.51 | 1.31 | 1.9 ±0.1 |
| 65 | 2.50 | 1.32 | 1.9 ±0.1 |
| 70 | 2.52 | 1.32 | 1.9 ±0.1 |
| 75 | 2.54 | 1.36 | 1.9 ±0.1 |
| 80 | 2.60 | 1.40 | 1.9 ±0.1 |
| 85 | 2.70 | 1.42 | 1.9 ±0.1 |
| 90 | 2.80 | 1.40 | 2.0 ±0.1 |
| 95 | 2.88 | 1.39 | 2.1 ±0.1 |
| 100 | 2.91 | 1.31 | 2.2 ±0.2 |

* The uncertainties were estimated from the scattering of points on the ionizing efficiency curves and do not include other uncertainties (see text).

appreciable contribution to the maximum height of the $H^+$ or $D^+$ peaks; such a behavior for $H_2$ was observed by Hagstrum and Tate[7] with a mass spectrometer of somewhat similar type. The shapes of our $H^+$ and $D^+$ peaks become less symmetrical above 32 volts, indicating some contribution of high velocity ions to the shoulders of the peaks. Thus all of our $R$ values should correspond predominantly to the production of monatomic ions by the single process of excitation of $H_2$ (or $D_2$) to $H_2^+$ (or $D_2^+$) in its lowest energy state. However, the possibility of smaller contributions from excited states of stable $H_2^+$ (or $D_2^+$) cannot be excluded.

We do not regard the apparent change of $R$ with electron energy in the table as significant, since a relative shift of about 1 volt in the absolute values of electron energy used for each related pair of ionizing efficiency curves, would be sufficient to account for the observed differences in $R$ between the low and high ends of the energy range. At these extremes the slopes of the ionizing efficiency curves are rather steep, whereas in the middle range of 50–90 volts, all curves are sufficiently flat to eliminate this source of error.

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## Strain in Non-Tetrahedral Carbon Atoms

C. A. Coulson and W. E. Moffitt
*Physical Chemistry Laboratory, Oxford, England*
January 23, 1947

In view of the recent correspondence in this journal[1–3] concerning the non-tetrahedral carbon atom, it seems desirable to call attention to certain results obtained by us which are now being prepared for publication.

Hybridization of $s$ and $p$ orbitals in carbon compounds was originally introduced to provide four atomic orbitals with strong directional properties, it being supposed that the attached groups were placed along the lines of greatest electron density. But, particularly in molecules which are "strained" in the original sense of Baeyer, we may expect that the lines of maximum charge density do not necessarily coincide with the directions of the attached atoms. In this way we are led to a treatment which regards the hybridization ratio $\lambda$ as a variational parameter. The energy $E$ of a molecule is expressed in terms of $\lambda$ and $E(\lambda)$ is minimized. This leads to the best possible description of the molecule in terms of the pure valence state approximation of perfect pairing. We have treated the molecules cyclopropane, cyclobutane, and cyclobutadiene along these lines, discussing their stability, strain energy, and the orientation in space of their hydrogen atoms. We have also considered the compounds spiropentane, cyclobutene, and dibenz-cyclobutadiene (diphenylene) with special reference to the earlier treatment of the cyclic $C_nH_n$ and $C_nH_{2n}$ by Penney.[4] It has also been possible to account qualitatively for the anomalous bond shortening associated with these strained systems[5, 6]—anomalous, inasmuch as it is associated with a decreasing force constant.[7–9]

Our chief results for cyclopropane may be summarized as follows:

(i) Each carbon atom is at the corner of an equilateral triangle and the hybridization is such (see Fig. 1) that the two orbitals from any one carbon, in the plane of the ring, make an angle of about 106° with one another. In this way there is obtained a gain of about 5 ev per $CH_2$ group over a model in which[1] this angle is set at 90°. This means that less overlapping of the wave functions of paired electrons is more than offset by a decrease in strain energy at the carbon atoms.

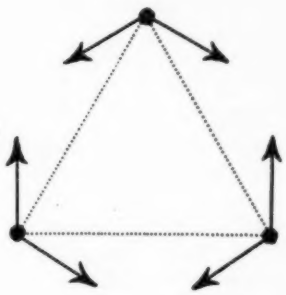

FIG. 1. Arrows denote directions of hybrid orbitals at the carbon atoms of cyclopropane.

(ii) The angle of 106° in the plane of the ring implies that the external valence angle should lie near 113°. A recent electron diffraction study[6] of the dichlorocyclopropane molecule gives 112°±4°.

(iii) The bond length is expected to be shorter and the C−C stretching force constant less than the corresponding quantities for, say, ethane.

(iv) The error caused by neglect of resonance in the plane of the ring—a neglect which distinguishes our pure valence state model from the full HLSP treatment—is estimated at approximately 1 ev per $CH_2$ group. This is important when discussing strain energies.

Since the C−C bonding orbitals are not directed at one another, these bonds may be described as "bent"—a concept which may be usefully employed symbolically to illustrate the effects (i)–(iv) above.

Our predicted HCH angle for cyclopropane (113°) differs appreciably from that of Duffey[1] (180°), and that of Kilpatrick and Spitzer[2] (122°), but is apparently in complete agreement with what is observed for the dichloro compound. Duffey's paper seems to contain no more than a restatement of the implications of Van Vleck's "$\omega$-model,"[10] whereas Kilpatrick and Spitzer's treatment, though much more enlightening, involves certain *ad hoc* assumptions which we have managed to avoid.

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## Electrolytic Behavior in the Presence of a Tension Impulsion

LUIS BRÚ VILLASECA AND CARLOS GÓMEZ HERRERA
*University of Seville, Seville, Spain*
January 30, 1947

WHEN a quick change is brought about in the magnetic field of an electromagnet, in which a conductivity vessel has been placed containing an electrolyte, a tension impulse occurs, which may be expressed as follows:

$$\int_{t_1}^{t_2} E \cdot dt = Q \cdot R,$$

where $E$ is the electromotive force, $t$ is time, $Q$ is the amount of electricity going through the solution, and $R$ is the resistance. Impulse being equal, the product $QR$ for an electrolyte shows a lower value than that estimated for the formula corresponding to a metallic conductor. The difference between both must be traced to an increase in the resistance of the electrolytic vessel, which appears when the flow of the current starts.

This increase has been studied by comparing the values of ordinary electrolytic resistances, measured on Kohlrausch's bridge, against those met with in the presence of a tension impulse, circuits based on Fucks[1] and Weasthone's being used. Tension impulses were in some cases of a magnetic and origin, and in the rest were brought about by applying a known tension for a small fraction of a second.

A number of sets of measurements have been made, in order to see the influence shown on this resistance increase by the physical and chemical factors which might be related to it. In order to avoid any polarizarion effect, non-polarizable electrodes were used, as well as a device to eliminate the influence of the duration of the former. The following results were obtained:

The resistance increase is independent of the presence of the magnetic field, of the effect of the vessel capacity,[2] of the amount of electricity going through the solution, and of the voltage applied, provided the latter is not very high. It only appears when the metal in the solution is different from that used as an electrode, and in the zone adjoining these, being greater in the cathodic region than in the anodic one. The smaller the surface of the electrode and concentration, the greater is the resistance increase; but its definite relation to the conductivity of the solution cannot be determined. Surface and concentration being equal and with salts of the same anion, it depends on the activity of the solution, showing the same values in the case of strong electrolytes.

The effect of the resistance increase cannot be traced as caused by any one of the following alone: polarizations of the various sorts, electrostatic capacities,[3] or overvoltage,[4] for in the case of any of these occurrences, it would depend on the charge going through the solution, as well as on the voltage applied to it. Nor is it brought about by relaxation of ionic clouds or by a change of the mobilities,[5] for it would then be a phenomenon of a general character.

The physical explanations of this effect having been discarded, it may be traced to the layer between the metal and the solution[6] brought about by reaction of both, the existence of which has been shown by various investigators. The resistance of this layer as the current begins to flow is greater than after it has flowed for some time, for in this case the stir caused by the alternating current will not allow it to recover its state of balance. This solution agrees with the results of all sets of experimental measurements.

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## The Formation of Per-Compounds in Relation to Electronegativities

M. HAÏSSINSKY
*Institut du Radium, Paris, France*
January 31, 1947

A LARGE number of chemical elements form, under the action of $H_2O_2$ (rarely by electrolytic oxidation), peroxides, per-acids, and per-salts of the Me−O−O− type, in which the valency of the element is not changed relative to that of the normal oxide or acid. When the element possesses several valencies (S, Cr, Mo, etc.), the valency in the per-compound is always the highest valency compatible with the position of the element in the periodic system, with the exception of nitrogen, for which the existence of a pernitrous acid ($N^{III}$) has been reported. The per-compounds are not well known from the structural point of view and their very existence is sometimes doubtful, but from their chemical behavior it is known that the bridge bond −O−O− is of the same nature as the −O−O− bond in $H_2O_2$ itself. In many cases an additional compound is probably formed by dipole-dipole action.

The following elements do not appear to form such compounds:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| (a) | Cl | Br | I | Se | Te | $As^V$ | $Sb^V$ | |
| | 3.0 | 2.8 | 2.5 | 2.3 | 2.1 | (2.2) | (2.1) | |
| (b) | $Ru^{VII}$ [1] | $Rh^{IV}$ | $Pd^{IV}$ | $Os^{VIII}$ | $Ir^{VI}$ | $Pt^{VI}$ | $Ag^{II}$ | $Au^{III}$ |
| | >2.4 | >2.4 | >2.5 | 2.5 | >2.4 | >2.2 | 3.2 | 2.9 |
| (c) | $Cu^{II}$ | $Tl^{III}$ | $Pb^{IV}$ | $Bi^V$ | $Mn^{VII}$ | $Co^{III}$ | $Ni^{III}$ | $Fe^{VI}$ |
| | 2.3 | 2.3 | 2.4 | >2.3 | 2.4 | >2.2 | >2.2 | >2.1 |

Group (a) contains metalloids and the corresponding numbers are the electronegatives calculated by Pauling[2] (except for As and Sb). Group (b) contains the noble metals, and group (c) other metals which show at least 2 degrees of valence.

I have calculated,[3] from thermochemical data, the electronegativities of these metals and of some others missing in Pauling's table with the aid of the equation of the latter:

$$Q = 23.06 \Sigma (x_a - x_b)^2 - 24.2 m_0.$$

I have shown in the course of this work that the electronegativities of the metals increase notably with their valency and that they are higher in oxides and fluorides

than in the other halogenides. The numbers given above in (b) and (c), as for As and Sb, are the electronegativities calculated from the heats of formation of the oxides.

The electronegativities of all elements which form per-compounds are generally smaller, rarely equal to 2.1, even in the oxide of the highest valency state.

From this statement and an examination of the numbers given above we can announce the following rule:

*The elements whose electronegativities are smaller or at most equal to 2.1 form per-compounds; those whose whole electronegativities are greater than 2.1 do not form per-compounds.* C (2.5), S (2.5), Hg (2.5), and N (3.0) are exceptions to this rule. Nitrogen presents another anomaly already mentioned (formation of a per-oxide of lower valency state).

The general rule can be easily accounted for if it is remembered that the electronegativity of hydrogen is 2.1. From the way in which the electronegativities have been calculated, it is to be expected that, for energetical reasons, the reaction

$$\mathrm{Me-O-.+H-O-O-H\rightarrow Me-O-O-.+H_2O}$$

will not be carried out if $x_{\mathrm{Me}}>x_{\mathrm{H}}$.

The exceptions require a more detailed study. Note that sulfur has already a very marked tendency to form bridge bonds in the polysulfides and polythionates;

$$\mathrm{Me-S-S\cdots-S_n^-},\quad \text{with}\quad n=1, 2, 3, 4.$$

[1] We will, consequently, not consider here compounds which are called peroxides or per-acids, but which form with valency change, e.g., $PbO_2$, $MnO_2$, $HMnO_4$, $HIO_4$, etc.
[2] L. Pauling, *Nature of the Chemical Bond* (New York, 1944).
[3] M. Haïssinsky, J. Physique **7**, 7 (1946).

## Selection Rules for Ionic Crystals

LUCIENNE COUTURE
*Laboratoire des Recherches Physiques, Sorbonne, Paris*
February 2, 1947

IN the appendix of his article[1] Halford gives the standard symbol for the space group, followed by the symbols describing the various sites; each of those symbols is preceded by the number of distinct sets of this kind and followed by the number of equivalent sites per set. (The numbers are appended only when they differ from unity.)

But when the site group is one of the following: $C_p$, $C_{pv}$, $C_s$, with $p=1, 2, 3, \cdots$, the number of distinct sets is infinite, for an axis or a plane of symmetry may contain several atoms belonging to different sets. Instead of $V_h^{16}$:$2C_i(4)$; $C_s(4)$, one should write: $V_h^{16}$:$2C_i(4)$; $\infty C_s(4)$.

In aragonite, the symmetry $C_s$ for $CO_3$ ions does not exclude the symmetry $C_s$ for Ca ions, which is the actual symmetry[2] instead of $C_i$. This will alter the theoretical conclusions: the lattice modes attributable to Ca ions are not forbidden in the Raman spectrum, and this, according to Halford's method, brings the number of lattice modes of aragonite up to nine.

I shall now discuss the validity of this method as applied to ionic crystals. In these crystals (in contrast to molecular crystals, e.g., organic crystals, rhombic sulfur) the number of Raman lines observed is often greater than the number deduced from Halford's method. For aragonite and cerussite this method permits 9 lattice modes in the Raman spectrum; experimental data give more lines, 12 for aragonite, 17 for cerussite (the general theory permits 18 lines). For barites, Halford's method gives 9 Raman lines caused by internal vibrations; the Raman spectrum actually contains 13 lines, a close approximation to the number of lines given by general theory which predicts 18 lines, 4 of them being very weak.

Moreover, the coupling of like vibrations between different ions of one set gives rise to distinct Raman lines; their polarization shows that the symmetry of the corresponding vibration is related to the whole symmetry of the unit cell. For instance: 1363–1377 $cm^{-1}$, Raman lines of internal vibrations for cerussite; 630–647 $cm^{-1}$, etc. . . ., for barites[3] 122.5–130 $cm^{-1}$, Raman lines of rotational vibrations of $ClO_3$ ions in $ClO_3Na$;[4] even in some molecular crystals there appear separations caused by the coupling: 46–54, 74–76, 109–127 $cm^{-1}$, in Raman spectrum of rotational vibrations for naphthalene.[5]

In the case of calcite, however, the selection rules obtained by Halford's method are in agreement with experimental data. This is due to the particular fact that the unit cell contains only two $CO_3$ ions which are symmetrical in relation to a center of symmetry. The theoretical conclusions are the same whether one takes the coupling into account or not. We have seen that this is not the general case.

Therefore, I conclude that, in ionic crystals, coupling of vibrations between the ions of a set cannot be neglected and that Halford's method, which is applicable to molecular crystals, cannot be applied to ionic crystals, even as a first approximation.

[1] R. S. Halford, J. Chem. Phys. **14**, 8 (1946).
[2] W. L. Bragg, Proc. Roy. Soc. London **A105**, 16 (1924).
[3] L. Couture, Comptes rendus **218**, 669 (1944); **220**, 87 (1945); **222**, 495 (1945); and also a paper which will shortly appear in Ann. de physique.
[4] A. Rousset, Comptes rendus **216**, 886 (1943).
[5] A. Kastler and A. Roussett, J. Phys. **2**, 49 (1941).

## Theoretical Interpretation of Vibration Frequencies of Paraffinic Hydrocarbons

G. B. B. M. SUTHERLAND AND D. M. SIMPSON
*Newnham and Pembroke Colleges, Cambridge, England*
February 17, 1947

IN a recent paper Ahonen[1] has calculated the normal frequencies of vibration for a number of octanes on the assumption of a valency force field. The values obtained are compared with the experimental data and although some degree of correlation is obtained, it would be difficult to apply these results to the discussion of the spectra of other paraffins. The purpose of the present note is to report briefly some calculations made during the war as part of a program of research[2] on the vibration spectra of hydrocarbons (primarily for analytical purposes), since these deal with certain skeletal frequencies common to many branched hydrocarbons and have therefore a wider application than the results of Ahonen.

Instead of attempting to calculate the frequencies of an isomeric series of hydrocarbons, we have concentrated on calculating the skeletal frequencies of certain structural units which are common to many paraffins. The particular

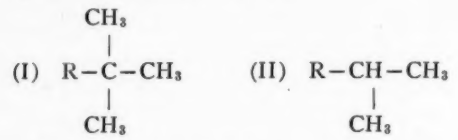
TABLE I. 2,2-dimethyl grouping.

| Hydrocarbon | | Characteristic frequencies in cm$^{-1}$ | | | | |
|---|---|---|---|---|---|---|
| Mass of Z | Name | Formula | Observed | | Calculated | |
| 15 | neopentane / 2,2-dimethyl propane | $CH_3 \cdot C(CH_3)_2 \cdot CH_3$ | 1250 | | 1288 | |
| 29 | 2,2-dimethyl butane | $CH_3 \cdot C(CH_3)_2 \cdot C_2H_5$ | 1214 | 1252 | 1225 | 1265 |
| 43 | 2,2 dimethyl pentane | $CH_3 \cdot C(CH_3)_2 \cdot C_3H_7$ | 1206 | 1250 | 1211 | 1261 |
| 57 | 2,2-dimethyl hexane | $CH_3 \cdot C(CH_3)_2 \cdot C_4H_9$ | 1202 | 1250 | 1203 | 1257 |
| 71 | 2,2-dimethyl heptane | $CH_3 \cdot C(CH_3)_2 \cdot C_5H_{11}$ | 1201 | 1250 | 1197 | 1254 |
| 85 | 2,2-dimethyl octane | $CH_3 \cdot C(CH_3)_2 \cdot C_6H_{13}$ | — | — | 1194 | 1252 |
| 99 | 2,2 dimethyl nonane | $CH_3 \cdot C(CH_3)_2 \cdot C_7H_{15}$ | — | — | 1191 | 1249 |
| ∞ | 2,2 dimethyl *n*-ane | $CH_3 \cdot C(CH_3)_2 \cdot C_nH_{2n+1}$ | — | — | 1177 | 1240 |
| | | | $\nu_3$ | $\nu_2$ | $\nu_3$ | $\nu_2$ |

TABLE II. 2-methyl grouping.

| Hydrocarbon | | Characteristic frequencies in cm$^{-1}$ | | | | |
|---|---|---|---|---|---|---|
| Mass of Z | Name | Formula | Observed | | Calculated | |
| 15 | isobutane / 2-methyl propane | $CH_3 \cdot CH(CH_3)CH_3$ | 1170 | | 1182 | |
| 29 | isopentane / 2-methyl butane | $CH_3 \cdot CH(CH_3)C_2H_5$ | 1170 | 1150 | 1180 | 1125 |
| 43 | 2-methyl pentane | $CH_3 \cdot CH(CH_3)C_3H_7$ | 1170 | 1145 | 1180 | 1116 |
| 57 | 2-methyl hexane | $CH_3 \cdot CH(CH_3)C_4H_9$ | 1170 | 1145 | 1180 | 1108 |
| 71 | 2-methyl heptane | $CH_3 \cdot CH(CH_3)C_5H_{11}$ | 1172 | 1145 | 1180 | 1101 |
| 85 | 2-methyl octane | $CH_3 \cdot CH(CH_3)C_6H_{13}$ | 1171 | 1143 | 1180 | 1095 |
| ∞ | 2-methyl *n*-ane | $CH_3 \cdot CH(CH_3)C_nH_{2n+1}$ | — | — | 1179 | 1085 |
| | | | $\nu_2$ | $\nu_5$ | $\nu_2$ | $\nu_5$ |

groupings we wish to discuss here are



(I) $R-C(CH_3)_3$ (II) $R-CH(CH_3)_2$

where R is any alkyl radical $C_nH_{2n+1}$, so that the molecules represented by I and II are 2,2-dimethyl and 2-methyl paraffins, respectively. It was found from data on infra-red spectra accumulated at Oxford and Cambridge that all hydrocarbons containing these structural units had strong, highly characteristic bands which appeared to be virtually unaffected by the remainder of the molecule. It seemed reasonable, therefore, to isolate such groups from the rest of the molecule and consider their internal vibrations as a separate problem, representing the remainder of the molecule R by a large mass. A simple valency force field was applied to these isolated units, the $CH_3$ and CH groups being treated as nuclei of mass 15 and 13, respectively. The most striking results are summarized in Tables I and II which give the frequencies of infra-red bands we found characteristic of the 2,2-dimethyl and 2-methyl groupings together with our calculated values. It should be emphasized that the pair of frequencies at 1250 and 1200 cm$^{-1}$ is found in all the more complex paraffins containing the 2,2-dimethyl grouping, e.g., 2,2,3- and 2,2,4-trimethyl pentane. Our main aim was indeed to establish the reason for the constancy of these characteristic frequencies rather than to give a complete interpretation of the vibration spectrum.

In the case of the 2,2-dimethyl compounds the model used was the $ZYX_3$ molecule in which $X$ is a mass of 15 ($CH_3$), $Y$ of 12 (C), and $Z$ a mass of $14n+1(C_nH_{2n+1})$. The six fundamental frequencies of such a molecule are conventionally numbered so that $\nu_1$, $\nu_3$, and $\nu_5$ are single parallel vibrations, while $\nu_2$, $\nu_4$, and $\nu_6$ are doubly degenerate perpendicular vibrations. Using this notation, the pair of frequencies at 1250 and 1200 cm$^{-1}$ are, respectively, $\nu_2$ and $\nu_3$, being derived from one of the triply degenerate frequencies of the symmetrical tetrahedral $YX_4$ molecule. This explains why these two frequencies coalesce into one in the case of neopentane. It will be noticed that the calculated values of the perpendicular frequency $\nu_2$ change by only 16 cm$^{-1}$ in going from 2,2-dimethyl butane to 2,2-dimethyl nonane whereas the parallel frequency $\nu_3$ is predicted to show a shift of 34 cm$^{-1}$ over the same range. Experimentally, $\nu_2$ appears to be virtually constant but $\nu_3$ exhibits a shift of 13 cm$^{-1}$ in going from 2,2-dimethyl butane to 2,2-dimethyl heptane. The calculations also suggest that there should be another characteristic frequency ($\nu_6$) near 420 cm$^{-1}$. Such Raman data as are available give some indication that this prediction is justified. The force constants employed were $4.65\times10^5$ dynes/cm for C−C stretching, and $0.45\times10^5$ dynes/cm for C−C−C bending. These clearly give too high a value for the triply degenerate frequency in neopentane and it seems probable, from this and other considerations, that both these constants should be somewhat lower in this particular molecule.

In the case of the 2-methyl compounds, the model employed was the $ZYX_2$ molecule (with $X$, $Y$, $Z$ defined as above). This molecule has six non-degenerate fundamental skeletal frequencies, of which $\nu_1$ and $\nu_3$ may be regarded as being derived from the parallel frequencies ($\nu_1^5$ and $\nu_3^5$) in the more symmetrical pyramidal molecule $YX_3$, while $\nu_2$, $\nu_5$ and $\nu_4$, $\nu_6$ arise from the splitting of the doubly degenerate pair which (following the usual conventional numbering) we may refer to as $\nu_2^5$ and $\nu_4^5$. Using this notation, the two frequencies near 1170 and 1140 cm$^{-1}$ are to be interpreted as $\nu_2$ and $\nu_5$, respectively, and correspond to the single frequency $\nu_2^5$ in isobutane. It will be noticed that, while the calculated value of $\nu_2$ stays virtually constant over the whole range of molecules considered, $\nu_5$ decreases slowly but steadily as the mass $Z$ is increased. On the experimental side $\nu_2$ is constant, while $\nu_5$ seems to show a slight decrease as $Z$ increases. No doubt a more exact theory would give better agreement on this point. In addition we find that there should be another characteristic constant frequency ($\nu_6$) near 400 cm$^{-1}$, but more experimental work is required to confirm this assignment. The force constants used were, for C−C stretching $4.5\times10^5$ dynes/cm, and for C−C−C bending $0.40\times10^5$ dynes/cm, i.e., somewhat less than those used for the 2,2-dimethyl paraffins. In view of the entire neglect of interaction terms we do not think these differences should be regarded as significant without further investigation.

[1] C. O. Ahonen, J. Chem. Phys. **14**, 625 (1946).

[2] This work which involved the spectroscopic examination of more than 200 hydrocarbons in the infra-red and ultraviolet was undertaken for the Ministry of Aircraft Production and the Institute of Petroleum by groups of workers at Oxford (under Dr. H. W. Thompson) and Cambridge (under Dr. G. B. B. M. Sutherland). The experimental results are now being prepared for general publication.

# Errata: Statistical Mechanics of Transport Processes II. Transport in Gases

[J. Chem. Phys. 15, 72 (1947)]

JOHN G. KIRKWOOD
*Cornell University, Ithaca, New York*

February 7, 1947

THE first line of Eq. (4) should read

$$\frac{\partial \bar{f}_i^{(1)}}{\partial t}+\frac{\mathbf{p}_i}{m_i}\cdot\nabla_{R_i}\bar{f}_i^{(1)}+\mathbf{X}_i\cdot\nabla_{p_i}\bar{f}_i^{(1)}=\sum_{l=1}^{\nu} N_l\nabla_{p_i}\cdot\Omega_{li}^{(1)}$$

with the time-averaged distribution function $\bar{f}_i^{(1)}$ appearing instead of the unaveraged distribution function $f_i^{(1)}$.

The second line of Eq. (8) should read,

$$\mathbf{p}_i'=\mathbf{p}_{i0}+\Delta\mathbf{p}_i(\tau).$$

The last sentence of page 74 should read: "By conservation of total linear momentum $\mathbf{p}_{i0}$ and $\mathbf{p}_{l0}$ experience increments $-\Delta\mathbf{p}^*$ and $\Delta\mathbf{p}^*$, respectively."

The last term in the brackets of the integrand on the right-hand side of Eq. (18) should be $\overline{f_i^{(1)}f_l^{(1)}}$ instead of $\overline{f_l^{(1)}f_l^{(1)}}$.